THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVI NOVEMBER 1951 No. 11

CONTENTS:

Bureau of Employment - - - - - - - - - - 585

Elections - - - - - - - - - - - - - - 586

Charles A. McNeil—Obituary - - - - - - - - 586

J. Earle McNutt—Obituary - - - - - - - - 587

By-Laws of the A. L. C. A. - - - - - - - - 588

Does Chloroform Extract Tannin from Vegetable Leather
By H. B. Merrill - - - - - - - - - - - 609

The Chemistry of Vegetable Tannins I. Quebracho
By R. C. Putnam and W. J. Gensler - - - - - - 613

Abstracts - - - - - - - - - - - - - - 641

SUBSCRIPTION: Members $10.00 a Year Non-Members $12.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
Acceptance for Mailing at Special Rate of Postage as Provided for in Section 1103.
Act of October 3. 1917, Authorized July 16, 1918

COPYRIGHT, 1951, THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Reliable Direct Sources the World Over

FOR

VEGETABLE TANNING MATERIALS

WATTLE EXTRACT
WATTLE BARK
MANGROVE BARK
MYRABOLAMS & EXTRACT
VALONEA & EXTRACT
DIVI DIVI
CUTCH
QUEBRACHO
SUMAC—LEAF & GROUND
TARA—PODS & POWDER
OAKWOOD EXTRACT, Swedish
LARCHBARK EXTRACT, Swedish

The OLSON SALES AGENCY

Import · Export

20 BROAD STREET (NEAR WALL STREET) NEW YORK 5, N. Y.

Cable Address:
"COROSAGE"

Telephones:
DIGBY 4-0226
0227

HAND-IN-HAND
—for 3 Generations

The makers of Gargoyle Leather Oils and Greases have worked closely with Tanners since 1866

It started when we made Vacuum harness oil—and we've been working closely with tanners ever since. Famous Gargoyle leather oils, greases and specialties are the results of our *85 years* of experience.

Today, we offer you—the services of skilled field technicians who are specialists in leather oils and greases, and in their correct application . . . research facilities and leather chemists to help solve your special problems . . . products made under the most exacting manufacturing methods to assure top quality.

Why not take advantage of our experience, technical facilities and products to improve *your* position?

SOCONY-VACUUM OIL COMPANY, INC.
Tanners Div., 26 Broadway, New York 4, N. Y.

SOCONY-VACUUM

GARGOYLE
Leather Oils and Greases

QUALITY AND SERVICE SINCE 1866

SPRUCE EXTRACT

POWDERED SUPER SPRUCE

LACTANX

■

Robeson Process Company

General Offices: 500 Fifth Avenue, New York, N. Y.

Operating Plant at Erie, Pa.

MECO EXTRACT

ONE GRADE—THE BEST

CHESTNUT WOOD EXTRACT

All Concentrations, Liquid to Dry Powder

Teas Extract Co.

6400 Centennial Boulevard

NASHVILLE 9, TENNESSEE

TENNESSEE PLANT
Nashville, Tenn.

ANDREWS PLANT
Andrews, N. C

Sterozol

Reliable Germicide and Preservative

Sterozol is a non-coloring, non-interfering liquid which can be used in any wet operation:

- For inhibiting microbial action on hides and skins in process
- For inhibiting mold on stock and leather in process
- For preserving finishes

Sterozol's low relative toxicity, ease of handling, and economy have contributed in a large measure to its acceptance in the trade.

Sebacol

. . . for dependable unhairing

Sebacol produces clean, uniform, quality leather under varied beamhouse practices.

Biobate

. . . for effective bating

Biobate provides controlled, effective enzymatic action during bating for all types of leather.

WALLERSTEIN COMPANY, INC.

180 MADISON AVENUE • NEW YORK 16, N. Y.

Better Leathers at Lower Cost ...

It's Easy With *Linco Products*

LINCO PRODUCTS

●

PANCREATIC BATES
FILLERS
SOLE LEATHER FINISHES
TANNER'S LIME
AND CHEMICALS

Do you believe the maintaining of leather markets desirable? If so, highest quality leathers at lowest possible cost are necessary. To accomplish this, no single improvement can be the answer but a lot of steps in the right direction might. Better yields is a very important step.

We invite your inquiries and permission to prove better yields with LINCO PRODUCTS.

L. H. LINCOLN & SON, inc.

COUDERSPORT, PA.

MANUFACTURERS AND DISTRIBUTORS OF TANNING MATERIALS
CONSULTANTS ON TANNING PROBLEMS

ARKO FAT LIQUORS

FORMULATED FOR PERFECT TAKE-UP AND NOURISHMENT

ARKO FAT LIQUOR L M:—Especially made for horsehide, cow sides glove and garment leather. Excellent for goatskin glove and garment.

ARKO FAT LIQUOR L C:—A superior oil for deer, pig, cape and cabretta glove leather.

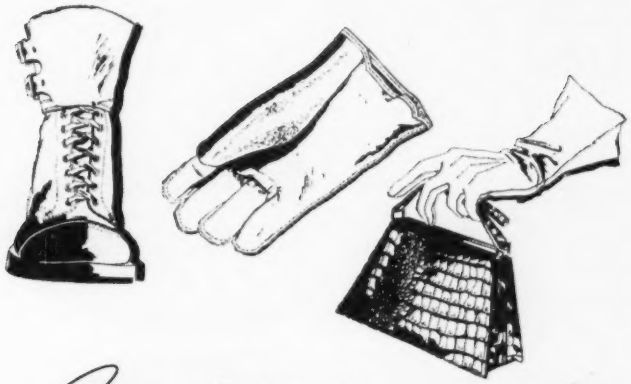
ARKO FAT LIQUOR C B:—Processed sulfonated cod oil for vegetable leathers.

ARKO FAT LIQUOR D:—For very fine suede leathers where dryness, nourishment and stretch are required.

Information, samples and demonstration upon request.

ARKANSAS COMPANY, Inc.
Newark, N. J.

Manufacturers of Industrial Chemicals for over 45 years



Made better with your leather

treated with Cyanamid's Tanning Specialties

These products are going a long way toward helping tanners raise processing efficiency, lower operating costs.

CUTRILIN® Bates . . . the pancreatic "bates of choice" in the tanning industry.

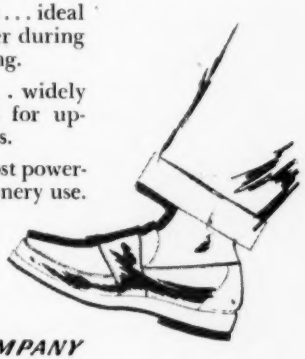
TWECOTAN® Tanning Extracts...*the* standard of excellence in tanning.

TANAK® Synthetic Tanning Agents . . . ideal for improving the quality of leather during both chrome and vegetable tanning.

TANAK® MRX Tanning Agent . . . widely preferred by experienced tanners for upgrading white and colored leathers.

BETASOL® OT Wetting Agent...most powerful wetting agent available for tannery use.

Let our staff help you make tests.



AMERICAN Cyanamid COMPANY

INDUSTRIAL CHEMICALS DIVISION
30 ROCKEFELLER PLAZA, NEW YORK 20, N. Y.
In Canada: North American Cyanamid Limited, Toronto and Montreal

Reduce your costs
Maintain quality

Outstanding control of microorganisms with SYNERGISTIC combinations of efficient bactericides and fungicides

For further details
See Bulletin 5L

BUCKMAN LABORATORIES, INC.

Manufacturing Chemists
Memphis 8, Tennessee

Representatives in Most Countries

MICROORGANISM CONTROL SPECIALISTS

QUALITY DYESTUFFS AND AUXILIARIES

A complete range of dyes for the coloring of all leathers • syntans for retanning and bleaching • mold preventives water repellents adhesives wetting, dispersing, emulsifying and finishing agents.

GENERAL DYESTUFF CORPORATION

435 HUDSON STREET · NEW YORK 14, NEW YORK

BOSTON • CHARLOTTE • CHICAGO • PHILADELPHIA • PROVIDENCE • SAN FRANCISCO

OUR 153rd YEAR

Natural Dyewood Products

Logwood

Fustic • Hypernic • Osage Orange

Produce level bottom shades for all colored leathers

•

Tanning Extracts

Dehydrated in the modern manner, perfect solubility, lowest cost

•

Coal Tar Dyestuffs, Synthetic Tans

•

NEW YORK COLOR & CHEMICAL CO. DIVISION

BELLEVILLE, NEW JERSEY

AMERICAN DYEWOOD CO.

285 MADISON AVENUE NEW YORK 17, N. Y.

Factories:
CHESTER, PA. BELLEVILLE, N. J.

Branch Offices:
BELLEVILLE, N. J. DANVERS, MASS.
CHICAGO, ILL. PHILADELPHIA, PA.
TORONTO, CANADA
MONTREAL, CANADA

SOLVAY
Ammonium
Bicarbonate

Improves the Quality of Your Leathers

...by penetrating the leather rapidly—raising the pH uniformly throughout the thickness of the hide.
...by maintaining the grain.
...by improving dyeing characteristics.

Specify SOLVAY AMMONIUM BICARBONATE for quality leathers!

Other Products for Tanners

- **CLEANSING SODA XX**
- **SNOWFLAKE* CRYSTALS**

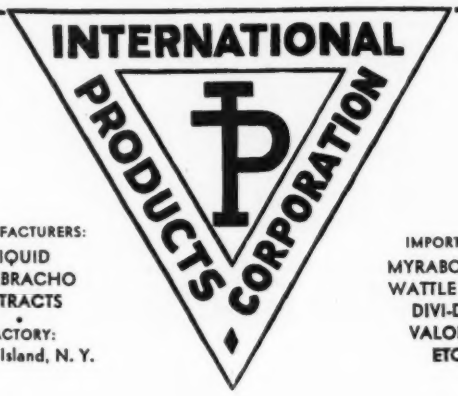
*REG. U. S. PAT. OFF.

SOLVAY Alkalies Chemicals 70 YEARS OF SERVICE 1881 1951

SOLVAY SALES DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 Rector Street, New York 6, N. Y.

BRANCH SALES OFFICES

Boston • Charlotte • Chicago • Cincinnati • Cleveland
Detroit • Houston • New Orleans • New York
Philadelphia • Pittsburgh • St. Louis • Syracuse



MANUFACTURERS:
LIQUID
QUEBRACHO
EXTRACTS
•
FACTORY:
Staten Island, N. Y.

IMPORTERS:
MYRABOLAMS
WATTLE BARK
DIVI-DIVI
VALONIA
ETC.

INTERNATIONAL PRODUCTS CORPORATION

29 BROADWAY 6, NEW YORK

Representatives:
San Francisco - London, Canada - Boston
Havana, Cuba - Mexico City, Mexico

"SUPREMO"
BRAND
SOLID-ORDINARY

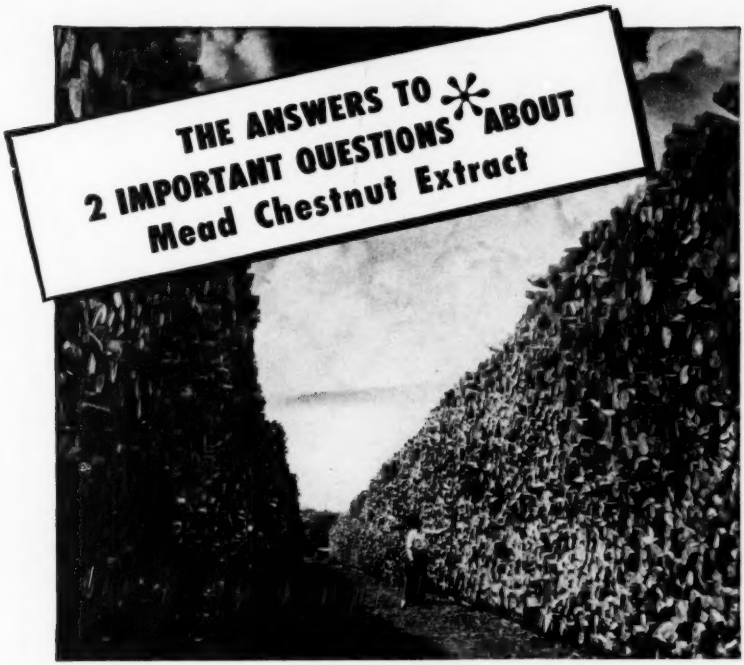
"LUNA"
BRAND
COLD WATER SOLUBLE

QUEBRACHO EXTRACTS

FACTORY AT PUERTO PINASCO, PARAGUAY

Sole Distributing Agents North America

VALONIA EXTRACT "S. E. N. S."



This is only a portion of the many stockpiles of chestnut logs that insure a continuous supply of Chestnut Extract.

1. Is the supply of Mead Chestnut Extract adequate?

Decidedly yes. Recent surveys show that there is enough chestnut wood in our forests to serve the leather industry for many years to come. Huge chestnut stockpiles, such as the one shown above, are converted under chemical control at five extract plants, insuring a steady supply of Mead Chestnut Extract.

2. Why is Mead Chestnut Extract preferred over other tanning agents?

Mead Chestnut Extract is a superior tanning material, made by America's largest producer of vegetable tanning extracts. Repeated experience has shown:

A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

IT'S A FACT!

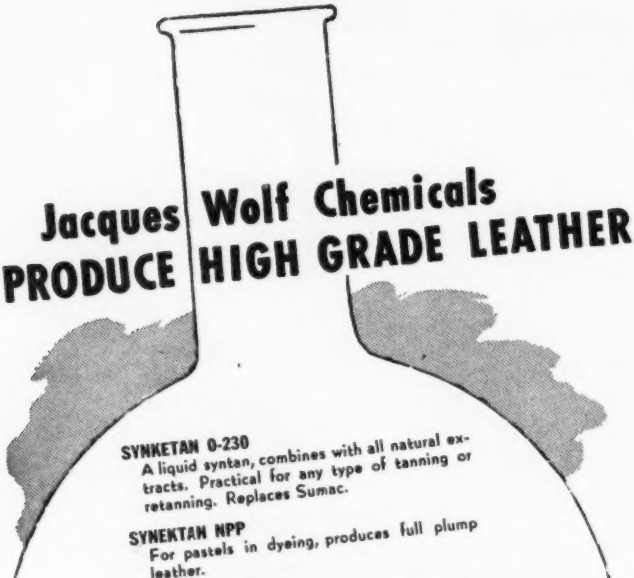
Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

MEAD
CHESTNUT
EXTRACT

THE MEAD CORPORATION
Tannin Extract Division, Lynchburg, Virginia



Jacques Wolf Chemicals PRODUCE HIGH GRADE LEATHER

SYNKETAN O-230
A liquid syntan, combines with all natural extracts. Practical for any type of tanning or retanning. Replaces Sumac.

SYNEKTAN NPP
For pastels in dyeing, produces full plump leather.

SYNEKTAN NCRP
In combination tannage; or in dyebath for chrome stock for better grain.

TANASOL NCO (Beads or Powder)
TANASOL D (Liquid)
With extracts, for lower costs and good color.

TANASOL PW (Beads or Powder)
Bleaching chrome stock; also on chrome stock for level dyeing and pastel shades.

SULPHONATED OILS (Various Bases)

MONOPOLE OILS (For Finishing)

EMULSIFIERS AND DETERGENTS
For good degreasing.

Samples and information upon request.

JACQUES WOLF & CO.
Chemicals
PASSAIC, N. J.

Plants at: Passaic, New Jersey • Carlstadt, New Jersey • Los Angeles, California

CchampionshipEleven

Dimethylamine. Synthetic form of nature's own accelerator of the unhairing process.

Oropon. Original and standard synthetic bate.

Leukanol. Synthetic tan assist responsible for popular acceptance of white leather.

Tamol. Dye assist which made pastel colors practical.

Zircotan. Produces through-white leather.

Primal. Resin dispersion giving outstanding flexibility in leather finishes.

Orthochrom. Pioneer washable leather finish.

Hydrholac. Aqueous emulsions of nitro cellulose lacquers.

Orotan. Industry-approved synthetic tanning material providing in itself a complete replacement for natural tannins.

Ortholite. Hard wearing lacquer finish of good flexibility at low temperatures.

Rhotex. The first synthetic product developed for pasting.

CHEMICALS FOR INDUSTRY

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

Representatives in principal foreign countries

OROPON, LEUKANOL, TAMOL, ZIRCOTAN, PRIMAL, ORTHOCHROM, HYDRHOLAC, OROTAN, ORTHOLITE, RHOTEX *are trade-marks, Reg. U.S. Pat. Off. and in principal foreign countries.*

AT YOUR SERVICE . . .

Let our

64 years of specialized experience work for you . . . profitably

ATLAS

Guaranteed **OILS**

- **NEATSFOOT OILS**
- **SULPHONATED COD OILS**
- **SULPHONATED NEATSFOOT OILS**
- **SPLIT OILS**
- **MOELLONS, and many specialty Products**

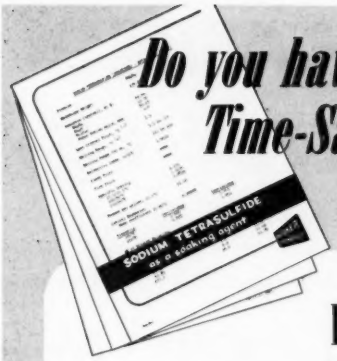
ATLAS REFINERY SINCE 1867 QUALITY LEATHER OILS NEWARK, N.J.

A Name and Symbol
Pre-eminent in the Tannery Industry

● For over half a century, ATLAS has been a leader in the production of Quality Oils for the Tanning Industry, through extensive research to serve you better. ATLAS specialized research, plus many years of practical experience in the production of consistently high-quality, guaranteed oils is your assurance of uniformity to meet definite specifications. Give your leathers the "quality look" with ATLAS Oils.

ATLAS *Refinery, Inc.*

142 LOCKWOOD ST. NEWARK 5, N. J.



Do you have this Time-Saving Data on Soaking?

TANNERS REPORT SAVINGS UP TO THREE DAYS

Skins soaked only 24 hours in water at 65° to 70° F., containing 0.7% Hooker Sodium Tetrasulfide, are sufficiently softened for drumming.

Even flint dried steer hides are frequently ready to process after only 48 hours in the same strength solution.

A 24-hour soak for green salted hides and skins, in 0.3% Hooker Sodium Tetrasulfide solution, gives cleaner hides, more uniform tannin distribution, a higher leather yield.

HOOKER BULLETIN 505 tells how tanners are cutting soaking time in half by using Hooker Sodium Tetrasulfide solution. It describes uses and advantages of this time-saving and money-saving new chemical. A request on your company letterhead will bring you a copy.

The Hooker technical staff, constantly at work on processing needs of the leather industry, is always on call for help in solving your particular problems.

HOOKER ELECTROCHEMICAL COMPANY

3 UNION ST., NIAGARA FALLS, N. Y.
NEW YORK, N. Y.
WILMINGTON, CALIF. • TACOMA, WASH.

CAUSTIC SODA • MURIATIC ACID
PARADICHLOROBENZENE • CHLORINE
SODIUM TETRASULFIDE • SODIUM SULFIDE

HOOKER CHEMICALS ®

10-1396

QUEBRACHO EXTRACTS

SOLID	LIQUID	POWDERED
STANDARD	SM	"PUREX"
BRANDS	SMS	SMS

PLANTS: NEWARK, N. J. — PEABODY, MASS.

ALSO

Tanning Extracts and Raw Tanning Materials from all parts of the world.

MYRABOLAMS	MANGROVE BARK
DIVI DIVI	VALONEA
TARA	SUMAC

WATTLE BARK
SOLID WATTLE EXTRACT
POWDERED MANGROVE and
VALONEA EXTRACTS

—IMPORTED BY—

THE

RIVER PLATE

IMPORT AND EXPORT CORPORATION

CHRYSLER BUILDING
405 LEXINGTON AVE., NEW YORK (17), N. Y.

BORNEO CUTCH

(MANGROVE BARK EXTRACT)

SAXE CUTCH CORPORATION

500 FIFTH AVENUE NEW YORK 18, N. Y.

UNIFORM TANNER'S OILS

for Every Type of Leather

MARDEN WILD CORPORATION

SOMERVILLE, MASSACHUSETTS

MARDEN WILD OF CANADA, LTD., HALIFAX, N. S.

LIGHT, EVEN-COLORED LEATHER

Many leather-processing men have found they can consistently get light, even-colored leather by standardizing on Sun's "Job Proved" Leather-Processing Oils. These oils mix easily. They do not form surface scum. They make it possible for the tanner to maintain uniformly high quality. They make it possible to process leather without frequent delays. For additional information, call your nearest Sun Office . . . or write to SUN OIL COMPANY, Philadelphia 3, Pa. *In Canada:* Sun Oil Company, Ltd., Toronto and Montreal.

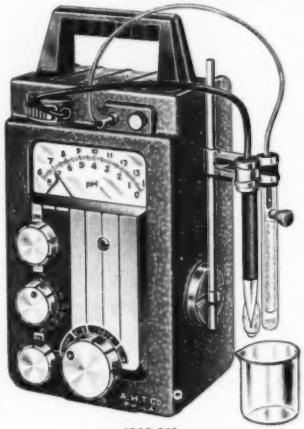
SUN PETROLEUM PRODUCTS SUNOCO

"JOB PROVED" IN EVERY INDUSTRY

NEW

BECKMAN MODEL N pH METER

PORTABLE – BATTERY OPERATED – RUGGED



4915-N1.

ADVANTAGES

Model N offers all the advantages of former Model M, which it replaces, and, in addition:

Subminiature electronic tubes (3), powered by hearing aid and flashlight batteries,

Built-in temperature compensation, 0 to 100°C, and

Light weight aluminum case (weight 7-½ lbs.), sealed and desiccated, with attached handle; convenient for laboratory, plant or field use.

BECKMAN MODEL N GLASS ELECTRODE pH METER, Battery Operated. A compact, direct reading instrument which uses the same basic circuit as Model M, which it replaces. With double, overlapping pH scale approximately 4 inches long reading in 0.1 pH division from pH 0 to 8 in red figures and from pH 6 to 14 in black; built-in temperature compensation 0 to 100°C; and control panel provided with "standardization" and "check" control knobs, switch for selection of range and "off", and humidity indicator.

Can be used in either vertical or horizontal position. Warm-up is rapid – approximately 10 seconds – permitting the instrument to be turned off between measurements, thereby saving battery life.

Furnished with sturdy 5-inch general purpose glass electrode and companion calomel electrode. Readings can be made rapidly with an accuracy of 0.1 pH over the range to pH 11, but greater accuracy is possible with careful operating technique. For use in the range pH 9 to 14, Type E glass electrode, with low sodium ion error, is recommended.

The various types of electrodes offered for use with Models M and H-2, including our 4923-F5 Electrode Conversion Assembly for volumes of only 2 to 3 ml, can all be used with Model N. Continuous readings can be made, and the instrument is convenient for making rapid acid-alkali titrations.

4915-N1. **Glass Electrode pH Meter, Beckman Model N-1,** complete with 5-inch glass and calomel electrodes, electrode holder, 50 ml Pyrex brand glass beaker, 1 pt. Buffer Mixture pH 7.0, 100 ml bottle saturated KCl solution, in case with handle **180.00**

4915-N2. **Ditto,** but with hinged double case providing carrying space for accessories required for field use **195.00**

More detailed information sent upon request.

ARTHUR H. THOMAS COMPANY

RETAIL—WHOLESALE—EXPORT

LABORATORY APPARATUS AND REAGENTS

WEST WASHINGTON SQUARE PHILADELPHIA 5, PA., U. S. A.

CABLE ADDRESS "BALANCE" PHILADELPHIA

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVI NOVEMBER 1951 No. 11

DEAN WILLIAMS ..... *Editor*

EDITORIAL BOARD

H. B. MERRILL R. B. HOBBS F. O'FLAHERTY
R. E. PORTER J. H. HIGHBERGER H. G. TURLEY

Only such correspondence as pertains to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Correspondence in reference to subscriptions, advertising and other business should be addressed to the Secretary, Dept. of Leather Research, University of Cincinnati, Cincinnati 21, Ohio.

Checks for subscriptions and advertisements should be made payable to the American Leather Chemists Association.

Subscriptions—Members, $10.00 annually; Non-members, $12.00 annually.

Published monthly by the American Leather Chemists Association.

Entered as Second-class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

Copyright, 1951, by the American Leather Chemists Association.

PAST PRESIDENTS OF THE A. L. C. A.

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VETCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. MCLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM.

OFFICERS 1950-'51

President—R. M. Koppenhoefer, Socony-Vacuum Laboratories, 412 Greenpoint Ave., Brooklyn 22, N. Y.

President-Elect—H. G. Turley, 501 Camden Ave., Moorestown, N. J.

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati 21, Ohio.

Council

Robt. B. Hobbs, Leather Division, National Bureau of Standards, Washington, D. C.

C. G. Telander, Armour & Co., Research and Development Dept., Leather Section, 500 Arch St., Williamsport, Pa.

A. W. Goetz, School of Leather & Tanning Technology, Pratt Institute, Brooklyn 5, New York.

W. Windus, 612 Warwick Road, Haddonfield, N. J.

C. M. Morrison, Jr., Reilly-Whiteman-Walton Co., Conshohocken, Pa.

BUREAU OF EMPLOYMENT

Position wanted as manager, assistant or chemist. Age 27, son of a leather merchant in Rumania. Trained in leather technology, experience in chrome leather manufacture. Now in Germany, wants position in America.

Address: R K - 100 c/o Secretary-A.L.C.A., University of Cincinnati, Cincinnati 21, Ohio.

ELECTIONS

ACTIVE

Philip L. Baxter, 330 Peck Street, Sault Ste Marie, Michigan.
Robert L. Cunningham, 2 Terrace Circle, Great Neck, L. I., N. Y.
Frank Faust, 936 Colborne Street, London, Ontario, Canada.
William Hook, American Hide & Leather, Inc., Ballston Spa, New York.
Yoshiyuki Inouye, Biochemical Lab., Dept. of Agriculture, Kyoto University, Kyoto, Japan
Herbert C. Miller, Jr., 41A W. Grant Street, Woodstown, New Jersey
Jerome J. Ritter, P. O. Box 343, Gloversville, New York.
Frederic A. Soderberg, 435 Hudson Street, New York, 14, New York.
George H. von Fuchs, 1221 Garfield Ave., Niagara Falls, New York.

Change to Active from Associate Membership

Frank Crystal, 549 W. Washington Blvd., Chicago 6, Ill.
Harry B. Hollander, A. Hollander & Son, 143 East Kinney Street, Newark, New Jersey.
Thomas A. Klein, 929 Lake Avenue, Racine, Wisconsin.

ASSOCIATE MEMBERS

M. L. Anderson, August Barth Leather Co., Box 88, New Albany, Indiana.
James W. Bell, 16 Monmouth Ct., Livingston, New Jersey.
Henry C. Chitwood, c/o Carbide & Carbon Chemical Co., P. O. Box N, South Charleston, West Virginia.
David W. Crookall, 19 Arlington Place, Arlington, New Jersey.
Woodrow D. Hawbecker, Hartnett Tanning Company, Ayer, Massachusetts.
John J. Hefferman, 12 Highland Street, Bradford, Massachusetts.
Fred Hilterhaus, 62 Bell Street, Bloomfield, New Jersey.
Albert J. Hulsebosch, 48 Walnut Avenue, Millburn, New Jersey.
Glenford W. Maybury, 142 Lockwood Street, Newark, New Jersey.
Oliver W. McKeown, 193 Vernon Street, Norwood, Massachusetts.
Francis J. Prescott, Chas. Pfizer & Company, 11 Bartlett Street, Brooklyn 6, New York.
Dhirendra Nath Sen, c/o Master General of Ordnance, M.G.O. Publication Section, Army Headquarters, New Delhi, India.
Morton W. Shepard, Jr., Geo. A. Shepard & Son, Bethel, Connecticut.
William Vroman, 5701 Tacony Street, Philadelphia 24, Pa.
Mrs. A. H. Winheim, International Leather Chemicals, Inc., Creve-Coeur (St. Louis), Missouri.
Harold J. Zahrndt, 85-73, 67th Avenue, Forest Hills West, New York.

Change to Associate from Student Membership

Herbert C. Breithaupt, Breithaupt Leather Company, Adams Street, Kitchener, Ontario, Canada.
John A. Lowell, Box 47, Dunstable, Massachusetts.

CHARLES A. McNEIL

Charles A. McNeil, former head of the Leather Laboratory of General Dyestuff Corporation of New York, died suddenly at his home, Hamilton, R. I., on Tuesday, September 18, 1951. He was born May 27, 1879, at

Hamilton, R. I. He was associated with General Dyestuff Corporation and its predecessors since 1900, and retired April 6, 1946. He was the son of a pioneer in leather processing in this country and though without benefit of a college education, Mr. McNeil studied chemistry under German experts at Frankfurt. Upon his return to the United States he contributed to scientific thought in the industry, and gave valuable assistance to the Government in two World Wars. He was active in Scottish affairs here and as a member of the American Leather Chemists Association since 1907 was held in high esteem by all who knew him. Through his long years of activity in the leather industry he had many friends and, it can well be said, he was universally liked and appreciated for his affability, integrity and outstanding ability in his line. He is survived by his widow and two sons.

General Dyestuff Corporation,
A. E. Hendershot, Treasurer.

J. EARLE McNUTT

On August twenty-third J. Earle McNutt died at Ridgway, Pennsylvania. He was born at Ridgway on January 29, 1886 and had lived there his entire life. Death, due to a heart ailment, came after an illness of several months.

On completion of his schooling at Ridgway, Mac began his life work in the Laboratory of the United States Leather company under W. H. Teas. At the time of his retirement on March 1, 1951 he had completed forty-seven years of faithful service and held the position of Assistant Chemist and Assistant Manager of the Hide Powder Division. He became a member of the Association in 1938.

Mac possessed those qualities so necessary to make a good analytical chemist: patience, imagination, careful and precise technique, a keen and inquiring mind, and above all, honesty. His work was largely in the field of tannin analysis and the preparation of hide powder. For many years he has been recognized as an authority in these phases of our activities. Through active participation in the work of Tannin Analysis Committees, he aided in the development of the official tannin analysis method and was instrumental in bringing about many of the refinements incorporated over the years. He conducted an extensive study on the effect of the weight of filter paper on analytical results, and collaborated with W. K. Alsop in developing the Alsop-McNutt dilution method for tan liquor analysis. He shared a large part of the control work necessary in the preparation of hide powder and was constantly working toward improving this reagent.

Mac maintained a keen interest in his community's civic and political affairs and in all form of sports, especially bowling.

His many friends in the Association have been saddened by his death. Those of us who were closely associated with him for many years feel deeply the loss of a true friend, and detect a touch of irony in that his passing should coincide with the closing of the laboratory of which he was such a large part and which to him meant so much.

J. F. Wagoner.

By-Laws

of

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

As revised and adopted June, 1940
with amendments to June, 1951

I. NAME

This Association shall be known as "The American Leather Chemists Association."

II. OBJECTS

The objects of the Association are:

1. To devise and perfect methods for the analysis and testing of leathers and all materials used in connection with their manufacture.

2. To promote the advancement of chemistry and other sciences, especially in regard to their application to problems confronting the leather industry.

3. To publish the results of investigations and researches dealing with the above objects.

4. To advance the professional welfare of its members by all legitimate means.

III. MEMBERSHIP

1. *Classification*:

The Association shall consist of:

(a) Active members.
(b) Associate members.
(c) Life members.
(d) Honorary members.
(e) Mutual members.
(f) Student members.

2. *Qualifications*:

(a) A candidate for election to active membership shall have had not less than six years of training and professional experience as a leather chemist, of which not less than two years shall have consisted of the successful pursuit of the study of chemistry or chemical engineering in an institution of recognized standing, and not less than two years shall have consisted of the practice of the profession of leather chemistry. This professional experience may include:

(1) Research in any field of natural science having a direct or indirect bearing on the manufacture or use of leather.
(2) The analysis and testing of leather or of any material of major importance in its manufacture.
(3) The direct technical supervision, in a responsible capacity, of any operation included in the manufacture of leather.

The candidate shall be actively engaged in one of the above occupations at the time his application is submitted. This shall not be construed to bar the election of a candidate, otherwise qualified, who is temporarily unemployed. In all cases of doubt, the Council shall be the sole judge of the adequacy of a candidate's professional training and experience.

(b) A candidate for election to associate membership shall be any person, not eligible for active membership, having a legitimate interest in the purposes of the Association.

(c) Life members shall be persons whom the Association desires to honor because of long and distinguished service to the Association.

(d) Honorary members shall be persons whom the Association desires to honor because of their outstanding contributions to science as related to the manufacture of leather.

(e) Mutual members shall be members in good standing of any foreign association of professional leather scientists, who shall have applied for mutual membership by virtue of a special agreement for reciprocal mutual membership entered into by this Association and the foreign association, as provided in Article IV.

(f) Student members shall be full time students majoring in leather or tanning chemistry or technology and pursuing a course of study of not less than twelve semester hours or its equivalent, registered in any accredited college, university, or other institution of learning above the level of high school or secondary school. The Council shall be the sole judge whether any institution of learning is accredited within the meaning of this section.

3. *Election of Members*:

(a) All members except mutual members shall be elected by majority vote of the Council. Mutual members shall be enrolled upon certification by the proper officer of the Society of which they are members, and payment of dues as set forth in Article VI, Section 1.

(b) Each candidate for active or associate membership shall be proposed in writing by two or more members, on a form provided for that purpose. This shall include associate members seeking transfer to active membership and former members desiring reinstatement. The form shall include: a statement, signed by the candidate, that he will, if elected, do his best to advance the objects of the Association and conform to its By-Laws; a statement of the class of membership for which application is made; the address and present occupation of the candidate; and a summary of his previous training and experience in sufficient detail to enable the Council to pass intelligently upon his qualifications. Each application shall be accompanied by the payment of one year's dues, except in the case of any member in good standing making application for a change in classification of membership.

(c) Applications for active, associate, or student membership shall be received by the Secretary, and shall be submitted by him to the Council for action, either at its next meeting or by mail vote, as provided in Article IV, Section 3. In case any application shall be rejected, no record of the fact shall be entered in the minutes. If the Council shall decide that an applicant for active membership is not qualified, by reason of occupation or lack of educational or professional experience, such applicant may be elected provisionally to associate membership, but shall be under no obligation to accept such election unless he so desires.

(d) Life and honorary members shall be elected by resolution of the Council setting forth the distinguished services for which such membership is conferred. This resolution shall be published in the JOURNAL of the Association.

(e) Each candidate for student membership shall be proposed in writing by one or more members, other than student members, on a form provided for that purpose. The form shall include: a statement, signed by the candidate, that he will, if elected, do his best to advance the objects of the Association and to conform to its By-Laws; a statment that the application is made for student membership; the address of the candidate and the name of the institution which he is attending; the expected date of graduation; and a statement from a dean, departmental head, or other responsible academic official, that the applicant conforms to the requirements of section III–2 (f), above, and is recommended for membership. Each application for student membership shall be accompanied by the payment of one year's dues, which shall be refunded if the candidate is not accepted for membership. A student member may renew his membership by submitting, with payment of annual dues, a statement that he is still qualified for student membership by virtue of being registered at an accredited institution of learning, as provided in Article III.

(f) Any associate member in good standing who becomes eligible for active membership may request that his classification be changed to active member. Any student member in good standing may, upon graduation from any accredited institution of learning, request that his classiffication be changed to associate member. Any such request may be approved by majority vote of Council.

4. *Privileges of Members*:

(a) Except as limited herein, all members shall enjoy the same privileges, including the right to attend and take part in all meetings of the Association, and to receive its JOURNAL and other publications.

(b) The right to vote, and to hold elective office, is restricted to active members, and to life members and honorary members who were active members when elected to life or honorary membership respectively.

(c) Life members and honorary members shall be exempt from payment of dues.

(d) A student member shall be entitled to receive the Journal of the Association, one copy of the By-Laws, and one copy of the "Methods of Sampling and Analysis". He shall be permitted to purchase other publications of the Association, which are sent to other classes of members, at a discount of 25 per cent from the prices charged to non-members for such publications. He shall not be entitled to sign nominating petitions for officers of the Association nor to sign a call for a special meeting. A student member may be appointed to serve on a committee of the Association, but shall have no vote in such committee.

5. *Termination of Membership*:

(a) All memberships shall date from January 1st. A new member shall pay dues for the full year in which he is elected, and shall receive all issues of

the JOURNAL for that year; *provided*, that the membership of a candidate elected after September 30th may, at his option, begin on the following January 1st.

(b) Any member may withdraw from the Association at the end of any year, by giving previous notice to the Secretary of his intention to do so, *provided*, that such notice, to be valid, must be accompanied by full payment of any indebtedness to the Association. By such notice and payment he shall be released from further liability as a member. No dues shall be refunded to any member wishing to terminate his membership before the end of the calendar year. Any student membership shall terminate at the end of any calendar year during which the student member ceases to be a full-time registered student as defined in III-2 (f). A student member who desires to become an active or associate member on termination of his student membership shall submit a regular application for active or associate membership, as provided in section III-3 (b) of these By-Laws.

(c) No person shall be entitled to the privileges of membership whose dues are unpaid. Any member whose dues are unpaid on March 1st of any year shall be so notified by the Secretary. Any member whose dues are unpaid on April 1st shall be dropped from membership.

(d) Any member who has been dropped for nonpayment of dues may apply for reinstatement. If the application is approved by Council, he may be reinstated upon payment of a reinstatement fee in addition to the dues for the current year. The reinstatement fee shall be three dollars if the reinstatement takes place in the same calendar year in which the member was dropped; if the reinstatement occurs in any subsequent year, the fee shall be six dollars.

(e) Any member guilty of gross professional or other misconduct, such as to bring the Association into disrepute by reason of his continued membership therein, may be expelled by vote of two-thirds of all the members of the Council, confirmed by vote of three-fourths of the members present at the next regular or special meeting of the Association; *provided*, that the member against whom such charges are brought shall be given a full and fair opportunity to defend himself before the Council and before the meeting of the Association; *provided further*, that such member shall be given the chance to resign before his case is brought before the meeting of the Association.

IV. MANAGEMENT

1. *Officers*:

(a) The management of the affairs of the Association shall be vested in a Council of seven members, a Secretary-Treasurer, and an Executive Secretary. The Council shall consist of a President, a President-elect, and five members of Council. The Secretary-Treasurer shall be an ex-officio member of Council and shall have no vote therein.

(b) The Secretary-Treasurer shall be appointed by the newly elected incoming Council at the beginning of its term in each even-numbered year.

(c) All the above officers and councilors (but not necessarily the Executive Secretary) shall be active members of the Association in good standing, elected as provided in Article V. They shall hold office for two years, reckoned from the adjournment of the annual meeting at which they were elected to the adjournment of the second annual meeting thereafter. With the exception of the President, all the named officers and two councilors shall be elected in even-numbered years, and three councilors shall be elected in odd-numbered years. In each even-numbered year, the office of President shall be automatically assumed by the President-elect of the preceding two years.

(d) The Executive Secretary shall be appointed by the Council, and shall be removable by the Council at the end of any calendar year, upon not less than sixty days' notice. The Executive Secretary shall be paid a salary, the amount of which shall be fixed annually by the Council. He shall devote such portion of his time to the business of the Association as the Council may consider a fair return for the compensation paid him.

(e) No person shall hold two positions in the Council. If any officer or Councilor is elected to fill a vacancy in some other office, his previous office shall thereby become vacant.

(f) All vacancies in the Council shall be filled by vote of the Council. The officer or Councilor thus elected to fill a vacancy shall serve until the end of the term of the officer or Councilor whom he replaces.

(g) No Councilor shall be eligible for reelection to a second consecutive full term as Councilor. This shall not preclude the election of a Councilor to the office of President-elect, or the election of a President whose term is about to expire to the office of Councilor.

2. *Duties of Officers*:

(a) The President shall perform the duties implied by his title, including (but not exclusively) the following:

(1) To preside over all meetings of the Association and of the Council, with full power to vote in both instances.

(2) To convene special meetings of the Council.

(3) To appoint committees and designate the chairman thereof, when so authorized by the Council, and to fill vacancies in committees, subject to the approval of the Council at its next meeting.

(4) To represent the Association in its relations with other scientific or technical societies, and with power to appoint a representative to act in his place.

(5) To appoint tellers as provided in Article V, and an auditing committee as provided in Article VI.

(b) The President-elect shall act for the President during the absence or temporary incapacitation of the latter, and shall act as Coordinator of Technical Committee Activity, in which capacity he shall perform the following duties:

(1) To serve as chairman of the Technical Committee Board, and to call at least one meeting of the board during each calendar year to review activities of the Technical Committees.
(2) To define, subject to approval by Council, the scope of Technical Committee assignments.
(3) To recommend or assign new problems to Technical Committes, and to suggest sub-committees for handling such problems.
(4) To assist Chairman of Technical Committee in the selection of members of sub-committees.
(5) To serve as the Technical Committees' representative on the Council and to propose to Council any actions necessary to promote Committee activity; to arrange, at the request of a Chairman of a Technical Committee, for space on Council's agenda for the presentation of Committee reports and the discussion of special problems of the Committee.
(6) To maintain a current record of the progress of assignments of Technical Committees.

On petition of the President-Elect or if for any other reason he is unable to serve, Council shall have power to appoint another of its members as Coordinator of Technical Committee Activities.

(c) The Secretary shall perform the duties usually performed by a secretary and treasurer, except those that are assigned to the Executive Secretary by action of the Council, including (but not exclusively) the following:

(1) To keep accurate records of all business transacted by the Association and by the Council, either at meetings or by mail ballot, and to publish a report of such business in the JOURNAL.
(2) To prepare and distribute all ballots, and to certify the results of all mail votings.
(3) To have custody of all funds of the Association, as provided in Article VI, and to countersign all checks for disbursements, unless the Council shall assign this duty to another officer.
(4) To keep, and publish annually, an accurate roster of the members of the Association.
(5) To receive applications for membership and transmit them to the Council for action, and to notify each newly elected member of his election.
(6) To notify each candidate for office of his nomination; each newly elected officer of his election; each member of a committee of his

appointment; each member of the Council of the date and place of each meeting; and each member of the Association of the date and place of each regular and special meeting of the Association.

(7) To collect all dues, and to notify each delinquent member of his suspension, as provided in Article III. To collect all other income due the Association, and to deposit all receipts to the account of the Association, as provided in Article VI.

(8) To keep a detailed record of all receipts and disbursements of the Association.

(9) To prepare the annual budget for submission to the Council.

(10) To make annual reports on the finances, membership and general condition of the Association, and such interim reports as may be called for by the Council.

(11) To have custody of the records of the Association, and to maintain an office at a place approved by the Council where such records may be kept and consulted. The cost of maintaining this office shall be paid by the Association.

(12) To execute contracts on behalf of the Association, when so authorized by the Council.

(13) To publish the Methods of the Association, as provided in Article IX.

(d) The Executive Secretary shall perform such of the duties of the Secretary as the Council may direct, subject to the following restrictions; all checks for disbursements must be countersigned by the Secretary, or by some other elected officer designated by the Council; all records of business transacted by the Association and by the Council, either at meetings or by mail ballot, shall be authenticated by the Secretary's signature; and all official notices and communications shall be issued in the name of the Secretary, over his signature.

3. *The Council*:

(a) Regular meetings of the Council shall be held (1) annually, during January or February, in such place as the Council may designate, to receive the annual financial report of the Secretary and to adopt the annual budget of the Association as provided in Article VI, and to transact any other business that may properly come before it, and (2) immediately after the adjournment of the annual meeting of the Assocation. Special meetings may be held upon call of the President or upon written request of any three members, at such times and places as may be most convenient to a majority of its members. Each member of the Council shall be notified in writing of each regular and special meeting at least ten days in advance.

(b) Four members shall constitute a quorum at any regular or special meeting. Unless otherwise specified in these By-Laws, all questions shall be decided by a majority vote of the members present and voting.

(c) Any questions arising between regular meetings of the Council may be submitted to a mail vote. Such questions shall be submitted in writing to each member of the Council, either by the President or the Secretary. The votes of members shall be received and counted by the Secretary. A majority vote of all the members of the Council shall be required to decide any question by mail vote. The poll shall be closed when a majority has been recorded either for or against the question at issue. The Secretary shall notify each member of the Council of the result of the ballot, and shall preserve the ballots for 30 days, during which time they shall be open to inspection by any member of the Council.

(d) The Council shall have all the powers and duties usually vested in the board of directors of a corporation, except as limited in these By-Laws, including (but not exclusively) the following:

(1) To adopt the annual budget of the Association and to authorize all expenditures by any officer or agent of the Association, as provided in Article VI; *provided*, that no expenditure shall be authorized that is not fully covered by the current assets of the Association.

(2) To establish and appoint Technical Committees, as provided in Article X, and other standing and special committees for any purpose conforming to the objects of the Association, as stated in Article II; to designate the chairman of such committees; or to delegate the appointment of any committee to the President.

(3) To elect all members of the Association as provided in Article III.

(4) To appoint the Editor of the JOURNAL; to fix his compensation; and to pass upon all contracts for the publication of the JOURNAL as provided in Article VIII.

(5) To appoint the Executive Secretary, fix his compensation, and assign his duties as provided in Section 1 and 2 of this Article.

(6) To appoint a nomination Committee for the nomination of officers and Councilors as provided in Article V.

(7) To fix the time and place of the annual meeting of the Association, as provided in Article VII.

(8) To consider and report on all proposed amendments to the By-Laws, as provided in Article XI.

(9) To receive reports from all officers and committees.

(10) To determine where the headquarters office of the Association shall be located, and to arrange for securing suitable office space.

(11) To enter into special agreements with foreign associations of professional leather scientists for reciprocal mutual membership, provided that any such agreement shall be terminable at will by either party to said agreement at the end of any calendar year upon the giving of reasonable notice of such termination.

(12) To appoint the Nominating Committee, as provided in Article V.

(e) All actions taken by the Council shall be published in the JOURNAL for the information of the membership. Any action on a matter not specifically delegated to the Council by these By-Laws may be annulled by vote of the Association at its next annual or special meeting.

(f) The Editor of the JOURNAL shall be notified of each meeting of the Council, and shall be privileged to attend such meetings and take part in all discussion, without the right to vote. The Council may extend this privilege of the floor to past officers, committee chairmen, or other members of the Association whose advice may be desired.

V. ELECTIONS

1. *General Provisions*:

The President-elect and Councilors shall be nominated by a Nominating Committee, or by petition, as hereinafter provided, and shall be elected by secret written ballot of the members eligible to vote.

2. *Nominations*:

(a) The Council shall, before each Annual Meeting of the Association, appoint a Nominating Committee, composed of three active members, to serve for one year. No officer or councilor shall be eligible to serve on this committee, and no member shall serve on two successive Nominating Committees. The composition of the Nominating Committee shall be reported to the membership at the annual meeting, and shall be subject to ratification by the active members there present. The Council shall designate the chairman of the Nominating Committee. Any vacancies in the Nominating Committee shall be filled by appointment by the President.

(b) The nominating Committee shall select two candidates for each office to be filled at the next annual election. The chairman of the Nominating Committee shall ascertain that these candidates are willing to serve if elected. The names of the candidates shall be reported to the Secretary not later than December 10th, and shall be published in the following February issue of the Journal of the Association.

(c) Additional candidates may be nominated by petitions, signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1st, and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

3. *Elections*:

(a) The Secretary shall prepare a ballot listing all the candidates nominated for each office in alphabetical order. This ballot shall be sent to each voting member at least thirty days before the date of the next annual meeting.

(b) Each member shall vote for one candidate for President-Elect (in even numbered years) and for as many candidates for Councilor as there are vacancies to be filled. Each ballot shall be enclosed in a sealed envelope marked, "Ballot Envelope." The ballot envelope shall bear no signature or other means of identification. The ballot envelopes shall be handed to the Secretary not later than 10:00 A. M. on the second day of the annual meeting, or may be mailed to reach the Secretary not later than the above date and hour. If mailed, the ballot envelope shall be enclosed in an outer envelope, and the outer envelope shall bear the hand-wirtten signature of the member voting.

(c) The Secretary shall check the ballots against the roster of members eligible to vote. He shall remove the outer envelope and deliver the ballot envelopes, unopened, to the tellers.

(d) The ballots shall be counted during the annual meeting by three or more tellers appointed by the President. The result of the election shall be announced to the membership during the annual meeting. The candidate for President-Elect who receives the greatest number of votes, and that number of candidates for councilor, equal to the number of vacancies to be filled, who receive the greatest number of votes, shall be declared elected.

(e) In case the ballot for any office results in a tie, the voting members, present at the annual meeting shall proceed to vote, by written ballot, on the names of the candidates so tied, and the candidate receiving the largest number of votes shall be declared elected.

VI. FINANCES

1. *Dues*:

(a) Dues shall be assessed against each member, in accordance with his classification as provided in Article III, and in accordance with special agreements between this Association and foreign associations for reciprocal mutual memberships as provided in Article IV.

(b) The dues for active, associate, and student classifications of membership shall be fixed by the Council, subject to approval by the active members at the Annual Meeting. Payment of dues shall entitle each member to all the privileges of his respective classification of membership as provided in Article III.

(c) Life members and honorary members shall be exempt from the payment of dues to this Association.

(d) In addition to the annual dues provided in this section, each member who holds mutual membership in any foreign association as provided in Article III shall pay such additional fee or fees as shall have been agreed upon by this Association and the foreign association or associations in which such member holds mutual membership.

(e) Each member of a foreign association who is a mutual member of this Association, as provided in Article III, shall pay an annual fee fixed by the special agreement between this Association and the foreign association, which fee shall entitle him to the privileges of mutual membership in this Association as provided in Article III. The amounts of the fees provided for in this paragraph and in paragraph (d) shall be recorded in the office of the Secretary and made known to any member on request.

(f) All dues charged to active, associate, and student members shall be payable to the Secretary on or before January first of each year. Dues charged to mutual members shall be paid to the proper officers of the several foreign associations not later than April first of each year.

(g) The Secretary shall, as of April first of each year, exchange lists of members from whom mutual membership dues shall have been collected, with the proper officers of the several foreign associations. Settlement of balances due to or from this Association and each of the foreign associations, as determined from such lists, shall be made on or before September first of each year.

2. *Classification of Funds*:

(a) The funds of the Association shall consist of a general fund, a JOURNAL fund, and other special funds established for specific purposes by vote of the Council.

(b) The JOURNAL fund shall be credited with all income derived from the JOURNAL, including advertisements, subscriptions to non-members, sales of single copies, volumes, reprints, etc.; and all expenses of publishing the JOURNAL, including the Editor's compensation, shall be debited against the JOURNAL fund. The Council may make an appropriation from the general fund for the support of the JOURNAL, which appropriation shall be transferred from the general fund to the JOURNAL fund, Any balance remaining in the JOURNAL fund at the end of any year shall revert to the general fund.

(c) The general fund shall be credited with all income of the Association, except JOURNAL fund income as described above, and except contributions for a specific purpose approved by the Council.

(d) Funds raised by committees for special and temporary purposes approved by the Council are not considered funds of the Association. This applies to funds contributed for entertainment at the annual meeting.

3. *Custody and Disbursement of Funds*:

(a) The Secretary shall collect all income due the Association, and shall deposit all receipts in a bank or banks approved by the Council. Such bank accounts shall be in the name of the Association. Such sums as are not required for current operations may be invested in interest-bearing securities

legal for trust funds under the laws of New York or Massachusetts, and previously approved by the Council.

(b) All disbursements shall be made by check. All checks shall be signed by the Executive Secretary, and countersigned by the Secretary, or by another officer duly authorized to do so by the Council. No disbursements shall be made except for a purpose, and within the amount, authorized by the Council, either in the annual budget or by specific appropriation.

(c) The Secretary, Executive Secretary, and any other officer authorized to sign or countersign checks, shall be under bond for the faithful performance of their duties. The amount of such bonds shall be decided by the Council. The expense of securing such bonds shall be paid by the Association.

(d) Any appropriation, except to cover a deficit in the operating expenses of the Association, which requires the expenditure of funds other than income received during the fiscal year in which the proposed expenditure is to be made, shall be submitted by the Council to the Association for approval. Such approval may be made by a majority of the members voting.

4. *Budget*:

(a) The fiscal year shall coincide with the calendar year. The Secretary shall prepare an annual budget with the advice and assistance of the chairman of the Ways and Means Committee (Section 6, this article) the Editor, and other interested officers. The budget shall be acted upon by the Council at its regular mid-winter meeting. Adoption of the budget, with or without amendment, shall be sufficient warrant for the Secretary to make the disbursements authorized therein.

(b) The budget may be revised, if necessary, at subsequent meetings of the Council, in accordance with variations in income of the Association.

(c) The budget shall appropriate to the support of the JOURNAL all the income that is automatically credited to the JOURNAL fund as provided in Section 2 of this article, and may contain an additional appropriation from the general fund for the support of the JOURNAL, if the Council shall so decide. If the income automatically credited to the JOURNAL fund shall exceed or fall below the amount estimated in the budget, then the amount made available for the JOURNAL in the budget shall be increased or decreased, respectively, in like amount without further action by the Council, except when the Council shall see fit to decrease or increase the appropriation for the JOURNAL from the general fund.

(d) The budget may annually appropriate to the support of the work of any Technical Committee or subcommittee, on request by the Coordinator of Technical Committee Activity, a basic amount not to exceed twenty-five dollars, for incidental expenses of such Technical Committee or subcommittee. The Chairman of the Technical Committee or subcommittee may expend as much of this basic amount as he considers necessary for the work

of his subcommittee or Technical Committee, and shall return any unexpended balance to the Secretary at the end of the fiscal year. Supplementary appropriations for the work of a Technical Committee or subcommittee may be made by Council, and shall be disbursed in the manner provided in Section 3 of this Article.

5. *Reports and Audits*:

(a) The Secretary shall submit to the Council, at its annual mid-winter meeting, a report showing the financial condition of the Association on December 31st of the preceding year, and a summary of receipts and disbursements for the preceding year. This report shall be supported by an audit, made by a licensed public accountant.

(b) An interim report, showing the financial condition of the Association, and a summary of receipts and disbursements for the year to date, shall be made to the Association at the annual meeting, at which time the books of the Association shall be audited by a committee of two or more members, not officers, appointed by the President.

(c) Both the annual and the above interim reports shall be published in the JOURNAL after acceptance.

6. *Ways and Means Committee*:

(a) To promote the financial welfare of the Association there is established a Ways and Means Committee. This committee shall consist of a chairman, appointed by the Council, and as many members as may be necessary, appointed by the chairman with approval of the Council. Appointments to the Ways and Means Committee shall terminate at the close of the annual meeting held in even-numbered years.

(b) The Ways and Means Committee shall aid in increasing the income of the Association by securing advertisers, new members, or any other proper financial support. The committee shall advise the Council and the Secretary regarding financial matters, and shall assist in the preparation of the annual budget.

VII. MEETINGS

1. *Annual Meeting*:

(a) An annual meeting of the members of the Association shall be held at such time and place as the Council may decide, for the purpose of electing officers, receiving reports, acting upon any other business that may be requisite or necessary, and listening to the presentation of papers.

(b) Notice of the time and place of each annual meeting shall be published in the JOURNAL at least two months in advance.

(c) All papers presented before the annual meeting become the property of the Association and shall be published in its JOURNAL unless released

by the Editor for publication elsewhere. With the approval of the Editor, papers may be published simultaneously in our Journal and in other scientific literature. When such paper has been presented at an Annaul Meeting a note to that effect will accompany its publication in both Journals.

(d) The business session of the annual meeting shall convene at 10:00 A.M. on the second day of the meeting, for the purpose of electing officers as provided in Article V, Section 4. The business session may be adjourned from day to day at the will of the members present.

(e) To assist in defraying the cost of the annual meeting, the Council may authorize the collection of a registration fee from members and non-members in attendance. The fee charged to non-members shall be not less than twice that charged to members other than student members; but this shall not include wives (or husbands) and minor children of members. The fee charged to student members shall not exceed half the fee charged to other members.

2. *Special Meetings*:

Special meetings may be convened by action of the Council, or by written request signed by at least fifty members of the Association. The call for a special meeting must state the business to be transacted and must be mailed to each member at least two weeks before the date set for such meeting.

VIII. JOURNAL

1. *General Provisions*:

For the furtherance of the purpose of the Association set forth in Article II (3), there shall be published the *Journal of the American Leather Chemists Association*, herein referred to as the JOURNAL. Unless the Council shall decide otherwise, this JOURNAL shall be published monthly.

2. *The Editor*:

(a) The JOURNAL shall be managed by an Editor, appointed by and removable by the Council.

(b) The Editor shall decide upon the suitability for publication of all articles submitted to him, except notices and reports, the publication of which is mandatory under these By-Laws. He shall be assisted in this duty by an Editorial Board, appointed by him with the approval of the Council, whose functions shall be advisory only. He shall secure bids for the printing of the JOURNAL, when so directed by the Council, and make recommendations to the Council regarding contracts. In making such recommendations it shall be proper for him to consider quality of workmanship and reliability, as well as price. He shall approve all bills incurred in publishing the JOURNAL before they are paid.

3. *Financial Control*:

All matters pertaining to the finances of the JOURNAL shall be decided by the Council, as provided in Articles IV and VI.

4. *Reprints*:

Authors of original articles appearing in the JOURNAL shall, upon request, receive 50 reprints of each such article without cost, and additional reprints at cost.

In calculating the cost of reprints, it shall be proper for the Editor to consider not only the price paid by the Journal for reprints, but also indirect costs properly chargeable to the function of furnishing reprints to authors, such as postage and office expenses.

IX. METHODS

1. *Definitions and General Provisions*:

(a) In accordance with Article II (1), the Association may adopt official and provisional methods for the physical and chemical testing of leather, or of any material used in producing it, or of any article of which leather forms a part.

(b) Official and provisional methods are intended (1) to provide means for the adjustment of differences between buyers and sellers, and (2) for the convenience of members and others in obtaining information regarding leather and related materials. Use of such methods to adjust differences between buyers and sellers shall be by mutual consent. Members using official methods in public analytical work are urged to state that fact in the report of the analysis or test.

An Official Method:

(c) An official method is one adopted as such after having been in use for at least one year as a provisional method, and that has been proved to give concordant results in the hands of different operators. No method shall be adopted as official unless data have been published, obtained by a committee of this Association or of another association of similar scope, that shows that the method does give concordant results.

A Provisional Method:

(d) A provisional method is a method in process of development, that has been so far perfected as to warrant its general use by the members of the Association.

(e) Each official and provisional method shall provide one, and only one, procedure for making a given determination or test. This shall not preclude the authorized use of two or more types of apparatus for a given test, if it shall have been proved that both or all types yield the same results. There shall be no "alternative" methods, except as provided in (f) below. The adoption of a new official method shall automatically repeal and annul any previously existing official method at variance therewith, and the adoption

of any new provisional method shall automatically repeal and annul any previously existing provisional method at variance therewith.

(f) When a proposal is made to adopt a *new method* to replace a previously existing official method, the new method, if adopted, shall become a provisional method, and shall be retained as a provisional method for not less than one year nor more than two years from date of adoption. During this period the old official method shall remain in effect, and either the old official method or the new provisional method may be used, as the parties interested shall jointly agree. In every case, the report of the analysis or test shall state which method was used. If the new method is adopted as official, after the elapse of not more than two years nor less than one year, the old official method shall be dropped; if the new method is not so adopted within the time limits specified, then the new method shall be dropped.

The probationary period prescribed above for *new methods* shall not apply to *changes in detail* of a previously existing official method. Such a change, if adopted, shall immediately become official, and anything in the method at variance with the change shall automatically be repealed and annulled. In case of dispute, the Council shall decide whether a proposed change constitutes a new method or a change in detail of an old method.

When a provisional method is adopted that deals with an analysis or test for which no official method exists, such method may be retained as a provisional method for more than two years, providing committee work is being done to improve such method before its adoption as official.

2. *Methods Committees*:

(a) The development of methods, and the consideration of all proposals to adopt, change, or discard any method, shall be in the hands of committees known as "Methods Committees", which shall be subcommittees of Technical Committees, as provided by Article X."

(b) Each committee shall convene at least once each year, at the call of its chairman.

(c) Any valid proposal or recommendation by a Methods Committee must be in writing and must be certified by the Chairman as having been approved by a majority of the members of the committee.

(d) It shall be the duty of each Methods Committee to conduct a continuous study of the methods of the Association in its particular field; to consider all published work bearing on these methods; to appoint sub-committees to investigate experimentally the accuracy and reproducibility of the results obtained by these methods, and the effect thereon of proposed changes, which sub-committees may include experts who are not members of the main committee or of the Association, but such experts shall have no vote; to coordinate the work of such sub-committees and to appraise their findings; to propose new methods and changes in existing methods; to consider and report upon

all such proposals originating outside the committee; and to submit to the Council an annual report of its activities, in time for such report to be printed in the issue of the JOURNAL next preceding the annual meeting of the Association.

(e) Any Methods Committee may enter into joint work with committees of other associations or societies, and may recommend the adoption by the Association of certain methods adopted by such other associations. This shall apply particularly to methods for the testing of materials that are used widely in other industries.

(f) Any member of a Methods Committee may appoint someone else to act as his proxy. Such appointment shall be in writing, and shall be subject to acceptance or rejection by the committee.

(g) Any member of a Methods Committee who, during any calendar year, takes no active part in the work of the committee, shall be automatically dropped from membership in the committee. An active part in the work of the committee shall consist either in carrying out assigned experimental work or in replying to correspondence.

3. *Adoption of Methods*:

(a) The following procedure shall apply to all proposals to adopt any new methods, to discard an existing method, (unless this is automatic as provided in Section 1 (f), of this article), to make an existing provisional method official, or to change any existing method.

(b) The proposal may be made (1) by majority vote of a Methods Committee or (2) by written petition signed by ten or more active members. All such members' proposals shall be referred to the proper Methods Committee for study. Each Methods Committee shall include in its annual report a definite recommendation regarding any proposal that was submitted to it not later than three months before the date of such annual report. If the report of the committee on the proposal is favorable, the proposal shall be acted upon like a committee proposal. If the report is unfavorable, the proposal shall be dropped, unless the recommendation of the committee is over-ruled by vote of the active members present at the annual meeting of the Association.

(c) The proposal shall be published in the JOURNAL previous to submission to the Association at its annual meeting.

(d) The proposal shall be brought before the Association at its annual meeting. The active members present at such meeting may recommend the acceptance or rejection of the proposal, or may order it returned to the committee for further study, or may receive the proposal without making any recommendation thereon.

(e) Unless the proposal is ordered returned to the committee, or unless the committee shall withdraw it following an adverse vote by the members

present at the annual meeting, the proposal shall be submitted to a mail vote of the active members. A ballot for such a vote shall be sent to each member not less than sixty days nor more than ninety days after the adjournment of the annual meeting. The ballot shall list the proposals to be voted upon, giving references to the number of the JOURNAL in which each was published, and stating any recommendations made by the members present at the annual meeting. Each member desiring to vote shall write "Yes" or "No" after each proposal, shall sign the ballot with his name, and shall return it to the Secretary within thirty days after it was sent out by the Secretary. The Secretary shall count the ballots, and shall announce the results by publication in the next issue of the JOURNAL. All proposals receiving the affirmative vote of a majority of the members voting shall become effective immediately upon publication of the results of the ballot.

4. *Compilation*:

(a) The Methods of the Association shall be compiled and published by a committee consisting of the Secretary, the Editor of the JOURNAL, and a third member appointed by the Council. This committee may rephrase or re-word any method to secure uniformity of style and clearness and conciseness of expression, but shall make no alteration resulting in any change in the authorized procedure.

(b) The methods shall be published in loose-leaf form. All new or changed methods shall be printed within thirty days after adoption by the members. New editions of all the methods shall be published at such times as the Council may direct. Each member shall be entitled to receive one free copy of each edition of the collected methods, and of each new or changed method. The price to non-members, and to members for extra copies, shall be fixed by the Council.

X. TECHNICAL COMMITTEES

1. *Establishment of Technical Committees.*

The Council shall have the power to establish and to discharge permanent technical committees. The coordinator of Technical Committee Activity shall recommend such action when, in his opinion, it becomes desirable, and shall define the field of work of each technical committee, subject to the approval of Council.

2. *Duties of Technical Committees*:

Each Technical Committee shall, within the field of work defined by the Coordinator of Technical Committee Activity, perform those duties assigned by the Coordinator including, but not necessarily or exclusively, the following:

(a) To take charge of the development and revision of methods as provided by Article IX.

(b) To conduct studies of technical problems concerned with leather manufacture and processing.

(c) To conduct studies of technical problems concerned with the standarization and specification of leathers and leather processing materials.

3. *Chairmen of Technical Committees*:

(a) There shall be a Chairman of each Technical Committee, who shall be appointed by the President, with the advice of the Coordinator of Technical Committee Activity, and subject to approval by a majority of the Council.

4. *Sub-Committees of Technical Committees*:

(a) A subcommittee of a Technical Committee shall be created as necessary to handle any problem, which shall have been assigned to the Technical Committee by the Coordinator of Technical Committee Activity. The subcommittee shall be nominated by the Chairman of the Technical Committee with the advice of the Coordinator of Technical Committee Activity, and subject to approval by majority vote of Council, and the Chairman of the subcommittee shall be designated by the Chairman of the Technical Committee.

(b) The size of a subcommittee shall be determined by the Chairman of its parent Technical Committee. In nominating members of a subcommittee, the Chairman of the parent Technical Committee shall give adequate representation, as far as practicable, to the tanning industry, to allied industries, and to independent laboratories, concerned with the problem. The Chairman of the Technical Committee may be a member of a subcommittee. An expert who is not a member of the Association may be a member of a subcommittee, but shall have no vote therein. A student member of the Association may be a member of a subcommittee, but shall have no vote therein. When two or more members of a subcommittee shall be representatives of the same company, independent laboratory or Government agency, they shall be entitled collectively to only one vote in the subcommittee.

(c) The duties of a subcommittee of a Technical Committee shall be such of the duties of the Technical Committee as apply to any problems that shall have been assigned to it by the Chairman of the Technical Committee.

(d) A subcommittee shall be automatically discharged when all its assignments are finished. An assignment shall be considered finished when Council or the membership of the Association shall have taken final action on a report of the subcommittee so as to dispose of its problem, or, if no action on the report is required, when the report shall have been presented to Council.

5. *Chairmen of Subcommittees*:

(a) The Chairman of a subcommittee shall be designated by the Chairman of the parent Technical Committee.

(b) The Chairman of a subcommittee shall have the following duties:

(1) To call and preside at meetings of the subcommittee.

(2) To be responsible for the assignment to subcommittee members of tasks involved in the study of the problems assigned to his subcommittee.

(3) To expedite the progress of the work of his subcommittee, and to render to the Chairman of the parent Technical Committee such reports on the progress of the work as may be required by the Chairman.

(4) To make such expenditures for incidental expenses from the annual budget of the subcommittee as he deems necessary.

(5) To present to the Chairman of the Technical Committee any reports or other matters requiring decision by the Chairman, the Coordinator of Technical Committee Activity, Council, or the Association.

6. *Technical Committee Board*:

(a) There shall be a Technical Committee Board which shall be composed of the Coordinator of Technical Committee Activity and the Chairman of all Technical Committees. The Coordinator shall be the Chairman of the Technical Committee Board.

(b) The Technical Committee Board shall meet at least once each year for the purpose of reviewing the scope of Technical Committee Activities, making recommendations relative to Committee jurisdiction on individual problems, on assignment of problems, and on such other matters as it deems necessary to expedite the progress of Technical Committee work.

(c) The duties of the Technical Committee Board shall be only advisory to the Coordinator of Technical Committee Activity.

XI. AMENDMENTS

1. Amendments to these By-Laws shall be submitted to the Secretary in writing, signed by ten or more active members. Each proposed amendment shall be referred to the Council for study. The Council shall render a report, recommending the adoption or rejection of the proposed amendment, at the next annual meeting of the Association, providing the amendment was received in time to be studied by the Council at its mid-winter meeting.

2. All proposed amendments shall be published in the issue of the JOURNAL next preceding the annual meeting, together with the Council's recommendation thereon.

3. All proposed amendments shall be brought before the Annual Meeting for discussion and vote. It shall be within the province of the members voting to adopt or reject such amendment, or to order that it be returned to the Council for further study or revision. Members unable to be present may record their votes for or against such amendment by notifying the Secretary in writing at any time before the amendment is brought to a vote. The total vote cast shall equal at least one quarter the number of the Active membership of the Association at the time the vote is taken. A two-thirds vote of the Active members voting, by ballot, shall be required to adopt an amendment.

Does Chloroform Extract Tannin From Vegetable Leather?

By HENRY B. MERRILL,

B. D. Eisendrath Memorial Laboratory
Racine, Wisconsin

Thirty-two years ago, an A. L. C. A. Committee headed by John Arthur Wilson [1] determined the quantity of material extracted from diverse leathers by 5 solvents, and found that petroleum ether removed the least and chlroform the most materials from every leather. The difference was slight for leathers fatliquored or stuffed with neutral glycerides, and greatest for leathers containing sulfated oil or oxidized oil (moellon). Some fatty constituents of leather evidently are not soluble in petroleum ether, and are not included in the fat as determined by the A. L. C. A. official method. Actually such constituents are included with fixed tannin as determined by difference.

A majority of the 1919 committee recommended changing the Official Method to require chloroform as extractant. This recommendation was repeated by a second committee in 1921 [2], but as considerable opposition developed no action was taken. However, in the 30 year interim, many laboratories have adopted chloroform as extractant, and this solvent is required by proposed Federal Specifications [3], based on a paper by Zimmerman and Pangborn [4].

One objection to the use of chloroform was a belief that this solvent extracts some tannin from vegetable leather. Qualitative tests [1] did show that tannin was present in the chloroform extracts of some vegetable leathers, but in view of the great sensitivity of such tests it remained an open question whether the quantity of tannin thus extracted was appreciable. The author has attempted to answer this question by making chloroform extractions of nearly fat-free, purified hide powders, tanned with four different commercial vegetable tannins and with a replacement synthetic tanning material (Orotan). The material, if any, extracted from such leathers would have to come

from the tanning material (of course it might be an impurity of a resinous or waxy nature rather than tannin), and conversely, if nothing was extracted, it would be a fair conclusion that the fat content of leather, determined by chloroform extraction, is not in error because of simultaneous extraction of tannin.

The results show that chloroform extracts little or nothing from fat-free collagen tanned with raw quebracho, chestnut, wattle, and eucalyptus, but does extract an appreciable quantity of material from a leather tanned solely with Orotan.

Materials: Delimed, acetone-dehydrated calf skin was ground in a Wiley mill, further treated with 4 changes of chloroform, and the retained chloroform evaporated at room temperature. A 5 g. sample contained 2.5 mg. (0.05%) of chloroform-soluble material. Portions of this hide powder were tanned for 5 days, in rotating bottles, with about 160% tannin, previously dissolved to make stock solutions that were clarified by sedimentation. The hide powder was first wet back, and half the tannin was added in 6 increments over a period of 4 hours. After 24 hours, half the liquor was drained off and replaced by the remainder of the tannin solution, which gave a final liquor containing about 6% tannin. Tannage in this strong liquor was continued for 4 days. Then the tanned powders were wrung out, and rinsed twice by suspending in water for an hour and wringing out. The object was to remove most of the excess tan liquor without washing out much loosely combined tannin. Portions of these leathers (Set *A*) were dried at room temperature; other portions (Set *B*), were further tanned for two weeks in fresh liquors containing 5% tannin, after which they were rinsed and dried like Set *A*. The aim was to secure as heavy a tannage as possible. The air dry leathers were analyzed for water and collagen. Since fat and ash were practically nil, tannin (including water soluble matter) was taken as 100 – (water plus collagen). The tannin contents per 100 collagen were: Chestnut *A* 104, *B* 112; Quebracho, *A* 87, *B* 92; Wattle, *A* 87, *B* 95; Eucalyptus (Myrtan), *A* 111, *B* 121; Orotan, *A* 89.

U.S.P. chloroform was used for most of the work. Some extractions of Orotan leather were made with A. C. S. reagent-grade chloroform, anhydrous chloroform, and other solvents. Non-volatile matter was determined in each solvent. For U. S. P. chloroform, the combined correction for chloroform-soluble matter in the untanned hide powder and non-volatile matter in the solvent was 1.5 mg.

Apparatus and Method: 3.00 g. samples of air-dry leathers were extracted with 90 ml. chloroform in A. S. T. M. extractors[4] for 2 hours or longer, following Zimmerman's procedure, except that paper extraction capsules were used instead of the prescribed metal extraction tubes. Because the residue weights were expected to be very small, the extracts were transferred quantitatively to weighed tannin dishes. The solvent was evaporated at

room temperature. The dishes and residues were heated in a forced-draft air oven at 100 - 105°C for one hour, cooled in individual desiccators, and weighed to 0.1 mg. The correction for non-volatile matter in the solvent, plus chloroform-extractable matter in the untanned hide powder, was applied to each residue weight.

Results: The quantities of material extracted by U. S. P. chloroform from the different leathers are given in Table I. It is evident that the maximum quantity extracted from any of the four vegetable tanned leathers is under 0.2% of the air dry leather, but that chloroform does extract considerable material (about 2%) from Orotan leather.

TABLE I

Extraction of leathers with U. S. P. Chloroform

Samples: 3.00 g. (air dry)
Solvent: U. S. P. Chloroform
Time: 2 hours

TANNED WITH	LEATHER A		LEATHER B	
	mg. residue (corrected)	% Air-Dry leather	mg. residue (corrected)	% Air-Dry leather
Chestnut	1.5	0.05	5.8	0.19
	1.7	0.06	3.4	0.11
Quebracho (raw)	0.1	none	2.3	0.08
	0.2	0.01	1.5	0.05
Wattle	1.0	0.03	5.6	0.19
	0.3	0.01		
Eucalyptus	−0.1	none	3.1	0.10
	0.5	0.02		
Orotan	59.3	1.98		
	56.2	1.87		

The Orotan residue was red-brown. Quebracho Leather *B* yielded a minute quantity of a bright lemon-yellow solid, presumably a flavone. The other residues were colorless, and bore no resemblance to tannin.

Further tests with Orotan leather (Table II) showed that practically nothing more was removed when the same samples were re-extracted for 2 hours with chloroform, or when the time of initial extraction was doubled. A. C. S. reagent-grade chloroform took out just as much material as U. S. P. chloroform; anhydrous chloroform took out a little less. Thoroughly washed and redried Orotan leather yielded almost as much chloroform extractable material as the lightly rinsed leather, indicating that the extractable material is not unfixed Orotan. Because of the known effect of small quantities of water on the stripping action of solvents [5], a sample of Orotan leather was dried over Al_2O_3 for 42 days before chloroform extraction. This reduced

the quantity of extracted material by two-thirds, but still the extract amounted to 0.6% of the air-dry leather.

TABLE II

Extraction of Orotan Leathers

Sample: 3.00 g. (air-dry)

SOLVENT	HRS. EXTRACTED	MG. RESIDUE (Corrected)	% of Air-Dry LEATHER	REMARKS
Chloroform U.S.P.	2	59.3	1.98	
" "	2	56.2	1.87	
" "	2	2.5	0.08	Further extractions of above samples
" "	2	1.4	0.05	
" "	4	50.1	1.67	
" "	4	50.9	1.70	Leather rewashed & air-dried.
Choroform A.C.S.	4	60.0	2.00	
"(Anhydrous)	4	49.6	1.65	
" "	2	20.3	0.68	Leather dried 42 days over anhydrous Al_2O_3
" "	2	18.9	0.63	
Benzene	4	19.6	0.65	
Petroleum Ether	2	2.1	0.07	
Ethyl Ether	4	25.0	0.83	

Benzene and ethyl ether extract about a third as much material from Orotan leather as does chloroform. Petroleum ether extracts less than 0.1%.

Conclusions: 1. The analytical result for fat, by chloroform extraction of leathers tanned with chestnut, quebracho, wattle, and eucalyptus is not appreciably affected by simultaneous extraction of tannin.

2. Chloroform does extract appreciable amounts of material from fat-free Orotan leather.

References

1. Extraction of Grease and Oil from Leather – Committee Report. John Arthur Wilson, Chairman. *J. Am. Leather Chemists' Assoc.*, **14**, 140 (1919).
2. Extraction of Oils and Greases from Leather – Committee Report, 1921. F. P. Veitch and I. D. Clarke, *J. Am. Leather Chemists' Assoc.*, **16**, 458 (1921).
3. Fed. Specif. KK-L-311, Method 6031 (1950); see also U. S. Army Specif. No. 9-97, 18 April 1944, applicable to vegetable tanned calf leather.
4. Zimmerman, E. W. and E. F. Pangborne. *J. Am. Leather Chemists' Assoc.*, **46**, 342 (1951)
5. Merrill, H. B., D. H. Cameron, H. L. Ellison and Cornelia P. Hall. *J. Am. Leather Chemists' Assoc.*, **42**, 536 (1947).

Received June 25, 1951

The Chemistry of Vegetable Tannins

I. QUEBRACHO*

By ROBERT C. PUTNAM and WALTER J. GENSLER**

Department of Chemistry,
Boston University,
Boston, Massachusetts

PART I

INTRODUCTION

An examination of our knowledge of the vegetable tannins reveals a dearth of exact chemical data. It was in the hope of clarifying one corner of this very broad field that the present study of the chemistry of quebracho tannin was undertaken.

No extensive body of work on quebracho tannin is available; and much of what is known is of doubtful value, at least as far as structure work is concerned, because of the questionable purity of the starting materials employed. Hence, one part of the present investigation was inherently exploratory. The plan of attack could not be predicted or charted beforehand with exactitude. It was anticipated that much effort would be expended in developing purification techniques. Then, using the purified material containing a minimum number of components, a chemical attack on the structural problem would be carried out. Data, covering such items as elementary analyses, molecular weights, solubilities, analyses for functionality, optical activities and so forth were to be collected. Such chemical conversions as methylation, acetylation and oxidation were to be performed and the resulting products carefully scrutinized.

In this way by collecting a body of facts about quebracho tannin, and by subjecting the data to analysis, a structure, or at least a molecular formula, was to be developed.

The work actually performed followed more or less the tentative plan. A major component of quebracho was isolated in what was considered a pure (or almost pure) state, and this material was subjected to extensive experimentation. A body of information was gathered concerning not only the original component, but also several of its derivatives and degradation products.

An attempt was made with some measure of success to relate the data so obtained to molecular formulas. It will be seen that the formulas so developed constitute an internally consistent framework onto which most of the

*Abstracted in part from the thesis of Robert C. Putnam presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Boston University.

**We wish to express our appreciation and thanks to the United Shoe Machinery Corp., Res. Div., Beverly, Massachu etts for defraying much of the expense incurred during this study, and for making its laboratories and other research facilities available for our use.

data may be fitted. It will be evident, however, that not all of the observations made are accommodated by the proposed formulas. Nor is it possible at this time to propose more than speculative structures for quebracho, basing the speculation in part on the results of earlier investigators. As the result of this work, however, much more is known about the main component of quebracho than ever before. A body of facts are now available which are trustworthy and which will be of assistance in future work in this field.

In 1854, Rochleder [1] pointed out the different colors given by tannins and their relation to the nucleus present in the molecule. Hlasiwetz [2] used this for a classification of tannins into three groups. One group contained the pyrogallol nucleus and gave a blue color with iron salts, a second contained the catechol nucleus and gave a green color with iron, and the third group gave the red color shown by phoroglucinol in the pinewood and hydrochloric acid test. Etti [3] and Perkin [4] showed that tannins containing the phloroglucinol nucleus may give the catechol test and that both tannins and plant dyes often have the same nuclei. Nierenstein [5] showed that Quebracho Colorado yields resorcinol (which gives a blue color with iron salts) and protocatechuic acid on hydrolysis and thus two color reactions could be given by the same tannin.

In 1918, Perkins and Everest [6] classified tannins into three groups:

A. Depsides or gallotannins (Contain ester groups).
B. Ellagitannins (Contain ellagic acid groups).
C. Phlobatannins

The behavior of each of these groups, which actually constitutes part of the criteria on which the classification depends, is as follows: [7]

1. With Ferric chloride
   A. gives a blue color
   B. and C. give a green color
2. With boiling dilute sulfuric acid
   A. gives gallic acid
   B. forms ellagic acid
   C. yields red phlobaphene precipitate
3. With pine wood and hydrochloric acid
   A. and B. do not react
   C. gives the phloroglucinol reaction
4. On alkaline fusion
   A. gives gallic acid and some pyrogallol
   B. yields protocatechuic acid
5. With formaldehyde and hydrochloric acid
   A. and B. do not react
   C. is completely precipitated

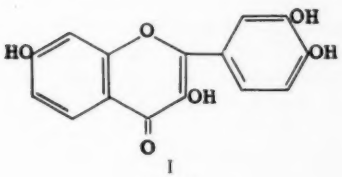
Freudenberg[8] then suggested a division of tannins into two main groups. The first two groups above he classified under one heading as hydrolysable tannins, i. e., hydrolysable by acids and enzymes.

This classification has been found to include depsides, gallic and ellagic acid glucosides and several esters of phenolcarboxylic acids with sugars and alcohols.

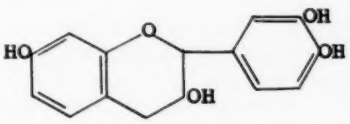
The second division includes those not hydrolysable by acids and enzymes and are termed condensed tannins. These give the typical phlobaphene reaction with dilute acid. This test consists of heating the tannin in a dilute acid solution whereupon an insoluble red precipitate is formed. Thus this class is also termed phlobatannin.

Freudenberg thought that phlobatannins were polymers of the 3-hydroxy polyhydroxy-flavan that gave fission products corresponding to those of the tannin. This idea was very attractive to Alfred Russell[9] and he felt that each tannin should have a corresponding 3-hydroxy polyhydroxy flavan. He recognized, however, that catechin was the only member of its class that had been identified as a natural product.

Because of the great similarity between anthocyanidins, flavones, flavanones, and flavonols, Perkin and Everest[6] thought that they must have some interrelation. Pick[10] found that in some plants the tannins disappeared as the anthocyanidins appeared. Freudenberg used the term catechin in a generic sense and since gambier catechin was a reduced quercetin, so he thought that fisetin must be the parent of a hypothetical quebracho catechin and so forth.



I
Fisetin



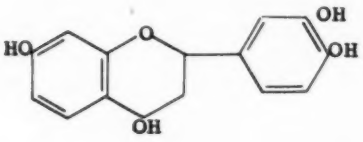
II
Hypothetical catechin

Perkin and Everest[6] showed that the fission products of phlobatannins were in general a phenol and a phenolic acid. Russell carefully analyzed two phlobatannins, hemlock and mimosa, and found the analyses to be in agreement with a pentahydroxy flavan. He thought they were 3, 7, 8, 3′ 4′, and 3, 5, 7, 3′, 4′ pentahydroxy flavan. He was unable to prove the tannins had these structures, however, and began to consider that perhaps the pyranoid hydroxyl might be in the 4 instead of the 3 position[11].

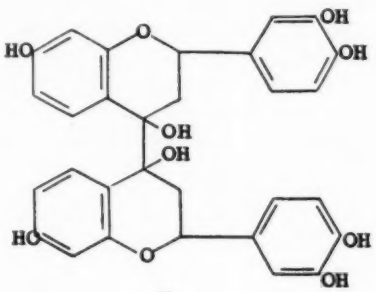
Russell assumed and subsequently found that the compounds he would have to prepare would be amorphous and hence only qualitative methods of comparison with natural products would be usable. Russell's general

method consisted, as an example, in the condensation of resacetophenone dibenzoate and protocatechualdehyde dibenzoate by means of anhydrous hydrogen chloride to give 2, 4, 3′, 4′ tetrabenzoyloxy chalcone, which was debenzoylated in a nitrogen atmosphere to the chalcone. This method was adopted to avoid the problem of trying to condense the unesterified compounds with their numerous hydroxyl groups and subsequent purification problems.

The yields by this procedure were poor and in certain cases the debenzoylation was found difficult, the chalcone tending to revert to its components. On reduction of the chalcone with zinc and dilute alcoholic acid he obtained a pink amorphous compound to which was assigned the structure of either 4, 7, 3′, 4′, tetrahydroxy flavan (III) or bis 7, 3′, 4′ trihydroxy flavpinacol (IV).



III



IV

He then compared the reduction product with natural phlobatannins by means of a series of color reactions and concluded that phlobatannins were of the same type structure. This procedure of preparation and testing was applied in several cases. He assumed that ring closure occurred during reduction since in the cases of 2-hydroxy chalcones having no other free hydroxyl group he found the product to be insoluble even in warm normal alkali. The hydroxyl groups in chalcones however, are not all of the same acidity and work by Valyashko and Rozum [12] has shown the ortho hydroxy group to be non-acidic and the parahydroxy group decidedly acidic.

Having assumed ring closure, Russell then considered that since the compounds were colored they must have been reduced, otherwise they would have been colorless and crystalline. This was a false assumption since a flavpinacol contains no chromophores. He also considered that the flavan structure was unlikely since similar benzopyran compounds are crystalline. Knowing that zinc and acid often give bimolecular reduction products he reduced chalcone itself and obtained a high melting compound which he concluded was of this type and confirmed his view by determinations of molecular weight. Furthermore, he measured the hydrogen absorbed in a closed system

and found it corresponded to that required for formation of a flavpinacol rather than for a flavan.

On treatment with alkali, quebracho tannin has been reported to give resorcinol and protocatechuic acid[5]. Russell considered that his (7, 3′, 4′ trihydroxy) flavpinacol was therefore the basic pattern present and ruled out the 5, 3′, 4′ compound since its type had not appeared in plant products. Recent work however, has revealed its presence in plants. Karrer and Schwab[13] isolated 5-hydroxy flavone from a deposit on the stalks and blossoms of *Primula imperialis* var. *gracilis*. Apparently this was the first case where a flavone having a hydroxyl group in the five and none in the seven position had been found in nature.

Russell and coworkers[9] synthesized a large number of derivatives having different phenolic patterns which they assumed were flavpinacols and found them qualitatively indistinguishable from the corresponding phlobatannins. They[14] then compared their ultraviolet absorption spectra with those of the natural products and found them in essential agreement. This may have been fortuitous inasmuch as the natural products are mixtures. The anhydrous alcoholic hydrogen chloride employed by Russell is a powerful condensing agent. Any compounds prepared by its aid should be subjected to a careful purification. His were not.

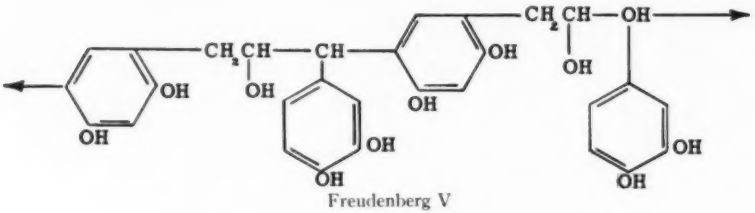
An actual scale model of a flavpinacol can be constructed but the hydroxyl groups are very crowded and the molecule has no freedom of rotation about the bond joining the two halves of the molecule.

Freudenberg[15] has severely criticized Russell's work on the following counts:

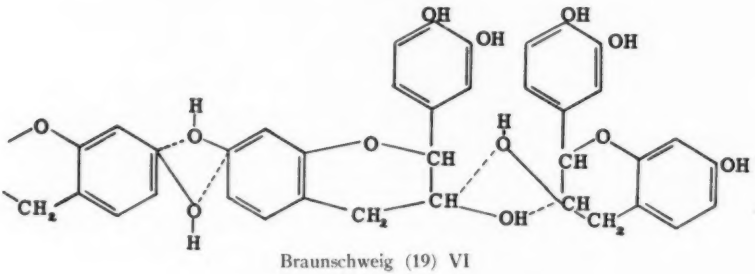
1. Products amorphous and ill-defined.
2. Difficulty of forming flavpinacols by reduction of chalcones.
3. Products must consist of numerous isomers.
4. Method of reduction productive of much selfcondensation.
5. Color reactions and absorption spectra dubious on mixtures.
6. Flavpinacols not found in nature.

Freudenberg favored the view that quebracho tannin had a catechin structure as its precursor. White[16] has recently (1949) investigated quebracho tannin by means of filterpaper partition chromatography and has found present five major components. One complex which comprises 39% of its tanning capacity he believes consists of flavones and flavone glucosides, not of catechins. He has criticized Freudenberg's[17] effort to formulate a hypothetical quebracho-catechin solely on the evidence of the presence of 1.6 parts of fisetin in 10,000 parts of extract.

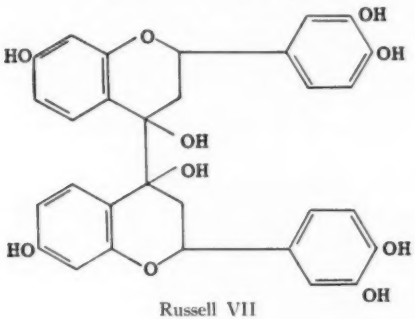
Shuttleworth[18] has discussed the structure of quebracho tannin and presented without proof some new possibilities based on the idea that it has a high molecular weight due to hydrogen bonding. He has listed the following structures:



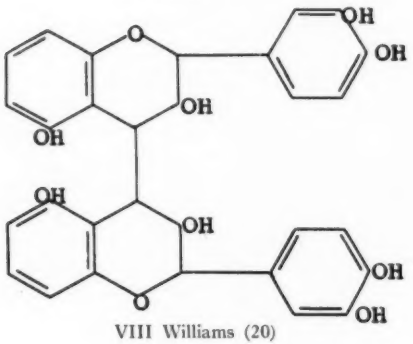
Freudenberg V



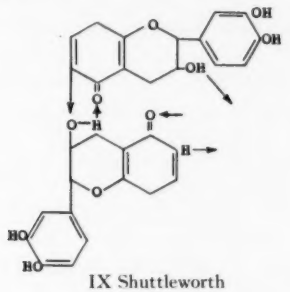
Braunschweig (19) VI



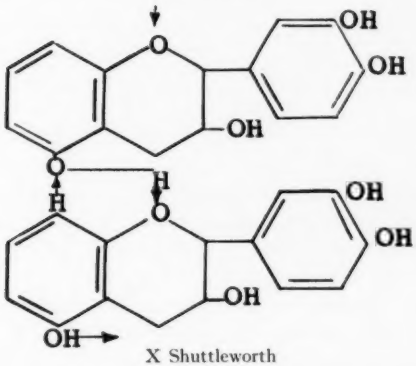
Russell VII



VIII Williams (20)



IX Shuttleworth

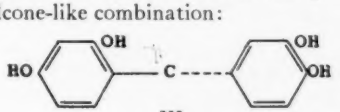


X Shuttleworth

Unfortunately past work on quebracho has not been characterised by a careful purification process carried out prior to degradation procedures. It is probable that many of the materials reported as present may have merely represented auxiliary substances. Much of the past work has involved speculation on structures based on minute quantities of isolated material and often the identity of this material has not been proved by preparation of derivatives.

Perkin and Gunnell [21] isolated small amounts of fisetin (a coloring matter), gallic acid and ellagic acid from quebracho. White [16] has carried out solubility and chromatographic investigations which have shown the presence of numerous ultraviolet fluorescing components, as well as other substances.

Jablonski and Einbeck [22] have reported the isolation of styphnic acid in 4.5% yield from quebracho tannin. Einbeck and Jablonski [23] claim to have isolated 3, 5 dinitro 2, 4 dihydroxy benzoic acid from quebracho and suggested quebracho was a chalcone-like combination:



XI

In turning to some molecular weight work, we find that in a discussion of factors influencing the tanning properties of tan liquors and extracts Humphreys[24] revealed the measurement of molecular weights of tannins by determining the freezing point depressions of the solutions at a given specific gravity. The apparent average molecular weight of quebracho was given as 1950. Since commercial quebracho is a complex mixture and each component in solution may be combined with varying amounts of other substances the number of solutes is unknown and the results cannot be used to arrive at any significant molecular weight figure.

Following this Douglas and Humphreys[25] determined by freezing point methods the apparent molecular weight of quebracho as 1159 before dialysis and 2421 after electrodialysis. Although the dialysis effected a separation, yet the tannin was by no means a single entity so the same criticism applies.

Compton[26] investigated the limiting pore diameter for quebracho extract by ultrafiltration methods in concentration of 0.5 to 2.0%. He found a value of 9-12 millimicrons and that there was no change in the value over the concentration range studied.

Stather and Laufmann[27] studied the influence of salting out methods on the total and the fixable tannin obtained in quebracho solutions by leaching out at different rates and temperatures. They found that quebracho was improved by heat.

Nunez[28] pyrolised quebracho extract under various conditions and claimed to have obtained hydroquinone, resorcinol, phloroglucinol and catechol.

Buchanan[29] and others reported a great deal of work done on the purification of tannins by four methods:

solvent purification
dialysis
precipitation
hide powder preparation

The solvent method employed by Buchanan was used in the present work. In summary, quebracho is reported to yield:

catechol
phloroglucinol
hydroquinone
resorcinol
protocatechuic acid
fisetin
gallic acid
ellagic acid
styphnic acid (with nitric acid)
3, 5 dinitro 2, 4 dihydroxy benzoic acid, (with nitric acid) and to have molecular weights 1950, 1159, 2421.

PART II

Discussion of Experimental Work

A. Purification of Quebracho[29]

The commercial extract (1900g.) was partitioned between the water and upper layer of an ethyl acetate, acetone and water mixture. This procedure has been reported[37] to increase the percentage of tannin present when analyzed by the standard method of tannin analysis as given in the American Leather Chemists Association's "Methods of Sampling and Analysis" (7,p.557). Considerable difficulty was experienced in separating the two jet black layers. After separation the upper layer was evaporated to dryness on a steam bath giving a yield in two extractions of 1,202.5g. This nearly black solid was then extracted continuously with ether for one week. The ether insoluble part was then treated with methyl isobutyl ketone at room temperature until no more dissolved. Nine-tenths of the ether insoluble material went into solution. The methyl isobutyl ketone was evaporated on a steam bath, and the residue oven-dried 2.5 hours at 109°C. giving 995g. of a red product A from 1900g. of starting material. For analytical purposes fraction A was further dried at 137°C. for two hours in a drying pistol. Observation of product A at elevated temperature showed that it starts to swell and lose vapor at 240°C. and begins to darken at 240°C.

Product A decolorised potassium permanganate solution and gave a smoky green color with ferric chloride solution in the same manner as the purified extract. This is indicative of a catechol nucleus.

The authors recognized early the necessity for having a method of determining the water content of the extract and its derivatives to aid in devising empirical formulas. This was further pointed up by the necessity of using a half molecule of water in working out some of the formulas. The Karl Fischer[30] method for water determination was employed after it was found to be satisfactory on such compounds as butein and phloroglucinol.

Product A was chromatographed on paper using butanol-acetic acid–H_2O. Most of the material appeared to have remained stationary as a brown spot. In ultraviolet a weak yellow spot having an Rf value of 0.11 and a strong yellow spot of Rf = 0.64 appeared.

A sample of product A dissolved in water was next passed through an anion exchange resin IRA400. One third of the material was retained by the resin. The product from the effluent was chromatographed on paper in butanol-propanol-hydrochloric acid giving the same two yellow spots at Rf = 0.14 and 0.65.

A sample of product A was then dissolved in acetone and passed through a column filled with aluminum oxide. Two-thirds of the material was retained by the column. The column showed a strong yellow band in ultra-

Analysis of product A showed the following:

	%	Av.	Calculated for $C_{21}H_{28}O_{11} \cdot H_2O$
C	62.70	62.81	62.62
	62.91		
H	5.48	5.35	5.09
	5.22		
N	0.67	0.65	
	0.62		
MeO	0.5	0.5	
	0.5		
H_2O	3.15		3.3
Rast M. W. (outside lab.)	237	222	594.6
	210		
	227		
	215		
Rast M. W. (the authors')	446 (Av.)		

violet light and the rest of the column had a brown color. Initial chromatograms of the effluent showed no spots but high concentrations did. It was possible that the fluorescing materials were minor components which always accompanied the major component.

A large quantity of product A was passed through the ion exchange resin with a view to effecting its further purification. The product B was insoluble in camphor. This was unexpected since product A was camphor soluble.

	%	Av.	Calculated for product B $C_{21}H_{28}O_{11}$-1.5H_2O
C	61.28	61.28	61.69
	61.28		
H	5.16	5.10	5.18
	5.03		
N	0.59	0.57	
	0.55		
MeO	0.5	0.5	
H_2O	4.05		4.47

The results indicated that the removed material had the same total composition as the unremoved.

A sample of solvent purified red extract (C) which had not had methyl isobutyl ketone treatment, but was otherwise prepared in the same manner as product A, was dissolved in acetone and adsorbed or caused to react with calcium oxide. After purification it was recovered with acid giving product D.

	Calculated for D		$C_{31}H_{28}O_{11}.2H_2O$		
	C 60.87	H	5.27	M. W.	612.6
Found	C 60.51	H	5.17	M. W.	317
	60.63		5.04	(outside lab.)	
	MeO 1.0			M. W.	525
	1.0			(the authors')	

It was evident that $C_{31}H_{28}O_{11}$ was a workable empirical formula and that the discrepancies could be attributed to the variable amount of water present and also to the nitrogen and methoxyl impurities which could not be removed. Since this formula appeared to satisfy both the solvent purified and calcium oxide adsorbed products and applied fairly well to the resin treated material, it was employed in the subsequent work.

B. Molecular Weight

Molecular weight determinations of substance A were carried out according to the Rast method and by the isothermal distillation method [32].

In the latter method, the observed molecular weight increased in value with increasing time instead of approaching a value asymptotically. Thus in fourteen days the molecular weight (in acetone) was found to be 430, in nineteen days 570 and in 25 days 746. The average molecular weight in camphor was found to be 222 by an outside laboratory, and 446 by the authors. These figures are not in agreement with the suggested molecular formulas. We can offer no explanation for the discrepancy, and have been forced to regard the values as anomalous. It will be noted subsequently that the Rast molecular weight determination of the methylated and acetylated substances are more in line with the values calculated from the postulated molecular formulas.

Investigators [25] in the field have concluded that phlobatannins have moderately high molecular weights. To obtain a qualitative idea of the molecular size, a series of dialytic experiments was performed to determine if the molecular weight fell in a high or low range. This work consisted of dialysing the extract in various solvents against the same and other solvents. In the course of a month up to 64% of the material dialyzed through a cellophane membrane of 0.0012 inch thickness without change of external solvent. No large changes in composition occurred.

Since the dialytic experiments indicated that not all of the material could be of high molecular weight, an attempt was made to molecularly distill the extract. At a pressure of less than 0.1 micron less than one milligram of sticky product was obtained by the time the extract C had carbonized. With the calcium oxide purified product D, nothing was obtained. A Rast molecular weight determination on the uncarbonized residue (Av. m. wt. 338) showed that the compound had not polymerized during the attempted distillation.

C. Methylation

Methylation experiments were performed to change the solubility characteristics of the purified extract and thus aid further purification and to determine the functionalities of the oxygen present. A further purpose was to limit the molecular weight possibilities since on the pure methoxyl derivative only whole numbers of methoxyl groups would be possible.

Many methylation experiments were performed on all the batches of extract in an effort to find the best conditions for obtaining the highest degree of methylation. Much effort was expended in a search for methods of purification of the derivatives. This was greatly hampered by the ability of the methylated derivatives to hold varying amounts of water and solvents so that melting points were indefinite. Only the most significant experiments will be discussed here.

It was found that initial methylation with diazomethane gave poor results. One early experiment, however, on a small (1 g.) sample gave an exceptional result which corresponded closely to the formula finally decided upon. The substance D though not soluble in ether was treated with diazomethane in ether. Most of the reaction product was insoluble. The soluble portion analyzed as follows:

Calculated for $C_{20}H_{14}O_{12}$, or $C_{21}H_{21}O_4(OCH_3)_7.H_2O$	C 65.80	H 6.39	MeO (7) 31.3
Found	C 65.80	H 6.06	MeO 31.1
	65.92	6.14	31.1

Unfortunately, this could not be repeated consistently nor done on a large scale. Experiments also showed that the use of dimethyl sulfate alone would not bring about complete methylation despite repeated attempts.

The next important experiment consisted of a series of methylations followed by a tedious purification which may be briefly summarized. Compound A (100 g.) was methylated with dimethyl sulfate initially at room temperature and subsequently at the boiling point of methanol. A second methylation was then performed entirely at the boiling point. The product was then treated with diazomethane twice. Following this it was then subjected to a complicated series of fractional precipitations with resultant division into a dozen portions. Of these, four were cream white in color and appeared of sufficient purity to warrant study. Their melting points and analyses were:

	MP.	Av. % H	Av. % C	Av. M. W.	% MeO
X–1	152–3	6.41	67.39	543	31.4
X–2	181–3	5.46	66.05	529	30.9
X–3	173–4	6.24	65.89	675	30.6
X–4	199–200	6.04	65.49	665	30.6

The ultraviolet absorptions of X-1 and X-4 were measured and found to show a maximum at 280 mμ with a density of 0.383 and 0.257 respectively in .001% (weight volume) concentration in alcohol. Infra-red spectrograms were next taken of all four fractions. X-2 and X-4 were identical. X-3 was the same as X-2 except for a very slight additional absorption of 5.83 μ. X-1 was the same as X-2 with an additional strong band at 5.83 μ and moderate band at 7.33 μ. The band in the 5.83 region is usually attributed to carbonyl adsorption. On further methylation of the four fractions, cream-white products having the following analyses were obtained:

	Av. % H	Av. % C	M. W.	% MeO	M P.
X-1-M	6.24	66.45	533	31.4	149.5-150.5
X-2-M	6.26	66.26	539	30.2	160–175
X-3-M	6.28	65.81	702	30.2	ca 202
X-4-M	6.28	66.45	648	30.2	185–6

The infra-red spectra of the compounds were now identical and the 5.83 μ and 7.33 μ peaks had disappeared. Analysis showed X-1 contained 1.20% water, X-4, 2.93%; and X-1-M contained 4.66% water. X-1-M absorbed at 280 mμ in the ultraviolet with a density of 0.242 in .001% concentration in alcohol. A molecular weight of X-1 was taken by the isothermal distillation method giving a value of 1310 after 83 days. A possible interpretation of the high molecular weight is the dimerisation of substance X-1 in acetone.

X-1-M may be compared with the formula:

$C_{21}H_{21}O_4(OCH_3)_7 - 0.5\ H_2O$

Calculated	C	66.76
	H	6.34
MeO	(7)	31.77
M. W.		683.7
H_2O		1.32

It did not agree in water content. The calculated molecular weight, although differing by 150 units from the observed Rast value is still in somewhat better agreement with the latter than the value calculated for a C_{18} molecule.

The entire methylation experiment was repeated beginning with substance A with certain improvements in the hope that a large batch of pure product might be obtained. After two dimethyl sulfate treatments and two diazomethane treatments, the nitrogen content was 1.55%. The methylated derivative was dissolved in methylal and chilled out in dry ice-acetone, filtered on dry ice and collected. It analyzed as follows (MA):

	Calc. (%)	$C_{31}H_{21}O_4(OCH_3)_7$–$0.5H_2O$ Found (MA) (%)	
C	66.76	66.68	66.45
H	6.34	6.47	6.40
N		0.26	0.29
Me (7)	31.77	31.0	31.0
H_2O	1.32	1.30	
M. W.	683.7	704, 655, 685, 668	(Av. 678)
End Me (No. of groups)		0.70	0.52

This appeared to be the purest product obtained. The substance had the lowest nitrogen content and agreed with the proposed formula.

Paper chromatograms of M A were run in butanol acetic acid-water, also in ethyl acetate–H_2O. No spot separations were observed in visible or ultraviolet with or without various developing agents. This may have indicated the removal of impurities or the removal of the function (phenolic hydroxy groups) responsible for fluorescence or color development.

In an effort to further increase the methoxyl content of the methylated derivative (MA), it was treated with silver oxide and methyl iodide. Instead of increasing the methoxyl content, the treatment resulted in a loss of one methyl group giving a product having the following composition:

$$C_{31}H_{22}O_5(OCH_3)_6–H_2O$$

D. Absorption Spectra and Optical Activity

An ultraviolet spectrogram of the calcium oxide purified material (D) was taken. It showed a single peak at 279 mμ with a density of 0.503 giving a logϵ=4.5 for a molecular weight = 612.5.

Absorption at 279 mμ in the ultraviolet was shown by all the purified batches and is shown by other phlobatannins[29]. Unpublished work has shown that 5, 3′, 4′ trihydroxy flavanone absorbs at 277 mμ. This peak may be due to the keto group.

Jarowski and Hess[31] have reported high log ϵ values for certain compounds having a keto group as follows:

2 carboxy, 5, 7 dihydroxy - chromanone
max. 283 mμ $\log \epsilon = 4.29$
2. 6 dihydroxy acetophenone
max. 271 mμ $\log \epsilon = 3.92$

In the infra-red, extract A showed a modest absorption at 5.83 microns in the keto region. On methylation and fractionation the methylated products showed varying absorption at this point, but one fraction showed very strong absorption. On further methylation with diazomethane, it completely lost its absorption at this point without change in methoxyl content. All the other fractions likewise lost their absorption at this point and all the spectrograms became identical.

The disappearance did not take place in the ultaviolet. The methylated fraction showing the powerful absorption at 5.83 microns in the infra-red showed a maximum at 280 mμ in the ultraviolet with a density of .383 in .001% concentration. On further methylation, although the infra-red peak disappeared the ultraviolet peak density only fell to .242.

The presence of a keto group was not indicated by any chemical test either in the extract or its methylated derivative. This was not proof of its absence, however, since the flavanones related to dracorubin[36] have been found to fail to respond to keto reagents.

Acetylation work, to be discussed subsequently, appeared to indicate that keto groups were absent.

A possible explanation for the ultraviolet absorption may be that the absorption is not due to a keto group, but is due to an ether linkage. Diphenylene oxide has an ether linkage. This substance has been shown[33] to absorb at 280 mμ giving a log $\epsilon = 4.2$. If the purified quebracho extracts contain a ring having an ether oxygen present, then this may be the cause of the absorption found. On methylation, should the ring oxygen be unaffected, then the absorption might well remain. Thus, the difference between the infra-red results and those obtained from the ultraviolet measurements can be explained by considering the absorption as being due to different factors.

A polarimetric study of the extract (A) was not possible due to the high color of its solutions. An investigation of the rotation of the methylated derivatives was made, however, although the absorption of light by the solutions made it very difficult. Readings using the sodium lines were made, but no readings could be obtained using mercury lines.

The methylated derivative X-1 which showed the strong 5.83 micron absorption in the infra-red showed a specific rotation of +9.4° at 26° in acetone and +12.3° in chloroform. X-3, which had a small absorption at 5.83 had a specific absorption of +13.2° in chloroform at a different concentration from X-1. The methylated derivatives of highest purity prepared in quantity (MA) had a specific absorption of +11.7° in chloroform.

The acetylated derivative had a specific rotation of +13.7° in acetone. Due to the difficulty of reading the polarimeter, these values may be one or even two degrees in error.

E. Acetylation Experiments

1. *Acetylation of Product A.*

Product A was acetylated in pyridine and an attempt made to purify the product by various methods including chromatography without success. Product A was reductively acetylated in acetic anhydride and after purification, the product was treated with acetyl chloride in dimethylaniline in order to ensure acetylation of any tertiary hydroxyl groups present in the

molecule. The white product (T) softened at 151°C and melted at 153–155°C. The analysis indicated that whatever formula was developed all the oxygen atoms were required for the acetoxyl groups.

Calc:	$C_{21}H_{17}(OCOCH_3)_{11}$				
	C 61.27	H 4.85	Ac 45.57	MW 1,038.9	
Found	C 61.48	H 4.54	Ac 46.49	MW 1,020	MeO 0.33
	61.77	4.68	46.82		0.47
	N 0.07				

This result indicated that either all the oxygen was present in hydroxyl groups or in groups changed to hydroxyl under the experimental conditions.

The acetyl derivative was definitely crystalline as shown by its X-ray diagram.

The preparation of the acetyl derivative was repeated in all details except that the zinc dust was omitted. The analysis showed no significant difference.

The results obtained by acetylation are among the most significant in the present work. This appears to be the first case where such a high acetyl content has been achieved with any phlobatannin. In addition, the method and the composition of the product appear to be general, for another phlobatannin, wattle, has been treated in similar manner. A product of similar composition was obtained. This will be discussed in a subsequent article.

The crystallinity of the product is very important. Past speculation on phlobatannins has usually led to the conclusion that they are polymers. The strength of this view with regard to quebracho is weakened by the dialysis previously mentioned. It is made ever less tenable by the crystalline nature of the acetyl derivative and the fact that it has a definite melting point (153-5°C) where as quebracho itself has no melting point and is not crystalline according to its X-ray diagram.

For a polymer to be crystalline, it has to have a very simple or very regular structure. If the molecular weight data on the acetyl derivative and also on the methylated compound are considered dependable, then they both point to $C_{21}H_{28}O_{11}$ as the basic formula for quebracho extract. This gives a molecular weight 576.5. Raffinose has been shown [26] to dialyse through a cellophane membrane of .0008 inch thickness comparable to that used with quebracho. The molecular weight of this sugar is 594 in crystalline form. It thus appears reasonable that a high proportion of quebracho extract is of moderate molecular weight and, therefore, not a high polymer.

This is the first case in which all the oxygen functions of a plobatannin have been utilized in derivative formation. If it can be demonstrated that no cleavage occurs during acetylation, the production of this derivative establishes that the often proposed structures [24] in which the molecule is represented as a polymer composed of units joined by ether linkages is untenable.

2. *Acetylation of the Methylated Derivative*

The methylated derivative (MA) of quebracho extract was subjected to the dual acetylation in order to discover if the remaining hydroxyl groups could be acetylated. The analytical results indicated that two rather than four acetyl groups entered the molecule:

Calc. $C_{42}H_{46}O_{13}$ or $C_{31}H_{18}O_2(OCH_3)_7(OAc)_2$								
	C	66.48	H	6.11	MeO	28.63	Ac 11.35	M.W. 758.8
Found	C	66.45	H	5.71	MeO	26.95	Ac 10.79	
		66.49		5.73		27.19	10.40	

3. *Deacetylation*

The completely acetylated derivative (T) was deacetylated by refluxing with potassium acetate with the loss of eight of the eleven acetyl groups. Potassium acetate in ethanol set up an equilibrium between acetate ion and ethoxide ion. Since phenols are in general stronger acids than ethanol, the conjugate base, phenolate anion, is a weaker base than ethoxide ion. In the equilibrium thus set up the acetyl group was lost to the ethoxide ion. Hence, it appeared that the fully acetylated product contained eight acetyl groups attached to phenolic or enolic hydroxyl positions and three to non-phenolic hydroxyls. Since the me hylated extract contained only seven methoxyl groups, it seemed that during acetylation one more phenolic or enolic hydroxyl group may have been generated, perhaps by the opening of an ether linkage. An alternate possibility was incomplete methylation.

F. Degradation Experiment

The methylated derivative (MA) was oxidized with alkaline permanganate and a 15% yield of pure veratric acid was obtained. It was identified by melting point and mixed melting point. Veratric anilide was prepared from it and identified by melting point and mixed melting point. Alkaline fusion of substance A gave 1.6% resorcinol, identified by melting point and preparation of its dibenzoate. The observations are in accord with those of Freudenberg and Maitland[17], who isolated veratric acid (25% yield) from one oxidation of methylated quebracho, and of Nierenstein[5] and Nunez[28] who reported resorcinol among the products obtained in the hydrolysis or the pyrolysis of quebracho. Certain other intermediate degradation products were obtained which will be discussed in a subsequent paper.

III. SUMMARY

The experimental work has provided the following information which may be briefly recapitulated.

A. Probable basic formula for the main constituent of quebracho:

$$C_{31}H_{28}O_{11}$$

This is proposed as the preferred formula, with the preference based on the fact that this formula can accommodate more of the assembled data than any other. Further work may lead to some revision of the number of hydrogen atoms or possibly even of the number of carbon or oxygen atoms. Consideration, however, of the data available shows that no great change *can* be made. The preferred formula either is the correct one or is a very close approximation to the truth.

B. Formulas for the methylated derivatives:

1. $C_{31}H_{21}O_4(OCH_3)_7$
2. $C_{31}H_{22}O_5(OCH_3)_6 \cdot H_2O$

C. Formula for the acetyl derivative:

$C_{31}H_{17}(OAc)_{11}$

D. Formula for the deacetylated derivative:

$C_{31}H_{28}O_8(OAc)_3$

E. Formula for the methylated and acetylated derivative:

$C_{31}H_{19}O_2(OCH_3)_7(OAc)_2$

F. Resorcinol obtained by degradation of the extract.

G. Veratric acid obtained by degradation of the methylated derivative.

H. One terminal methyl group found present in the extract.

I. Methylated and acetylated derivatives found to be optically active.

J. Certain intermediate breakdown products obtained by oxidation, fusion and nitration (to be discussed in a later paper).

The formula for the undecacetyl derivative shows that all the oxygen in this compound are required for the acetoxyl groups. This indicates that all the oxygen in the original substance either existed as hydroxyl groups or were converted to such during acetylation. One possibility is the presence of ether oxygen. Perkin and Hummell[35] have shown that flavanones easily isomerise to chalcones with the resultant conversion of the ether oxygen to an hydroxyl group. Such a process would generate a double bond. The acetyl derivative does not absorb bromine and there appears to be no explanation of this fact.

This derivative indicated $C_{31}H_{28}$ as the basic structure. The deacetylated product contained only three acetyl groups and this seemed to show that three hydroxyl groups differed from the other eight.

Certain intermediate breakdown products have been isolated some of which offer a promising line of attack for future work, and these will be discussed subsequently.

Similar work has been performed by the authors with wattle and a dodecacetyl derivative prepared. The close relationship of wattle and quebracho will be mentioned in a subsequent paper.

PART IV

Experimental

Key

A—Extract purified by acetone, ethyl acetate, ether and methyl isobutyl ketone.
B—Extract A passed through ion exchange resin.
C—Extract purified by acetone, ethyl acetate and ether.
D—Extract C purified by calcium oxide treatment, X-1, X-2, X-3, X-4—Fractions of methylated A. X-1-M, X-2-M, X-3-M, X-4-M—The above methylated once more.
MA—Extract A methylated in large quantity.
T—Acetyl derivative.

A. Isolation of Substance A From Quebracho By Solvent Treatment

A total of 1900 gm. dry ground quebracho extract obtained from the American Oak Extract Co. was rotated in a bottle for 6 hrs. in four batches using the following proportions of solvent[29]:

500 gm. quebracho extract
700 cc. water
750 cc. Acetone
1500 cc. ethyl acetate

The layers were separated using a strong light to help locate the interface and each evaporated to dryness on a steam bath, the solvent layer yielding 1,070 gms. A second solvent extraction of the solid from the water layer gave 132.5 gms. more. The solid from the solvent layer was ground very fine and extracted in a Soxhlet apparatus with ether for one week. The solid was allowed to dry and then permitted to stand at room temperature in contact with methyl isobutyl ketone until no more material dissolved (one week). The undissolved portion was filtered and further treated until no more solution occurred. The methyl isobutyl ketone was evaporated on a steam bath and the solid further dried in an oven for 2.5 hrs. at 109°C.

B. Preparation of Substance D From Substance C by the use of Solid Calcium Oxide

Substance C (20 g.) was dissolved in 300 cc. acetone, 12 g. calcium oxide was added, then 60 cc. water was stirred in. The solution gradually changed

from a red color to a muddy color. This was taken to indicate a slow absorption of the dissolved material on the calcium oxide. The precipitate was filtered, washed with acetone and suspended in 400 cc. water. The suspension was stirred to dissolve any soluble material, filtered and again washed with water. The precipitate was then suspended in 400 cc. water and a solution of 55 cc. glacial acetic acid dissolved in 80 cc. water gradually added. Following this, 25 cc. concentrated hydrochloric acid was gradually added to bring the pH to 1 or until nearly all the precipitate had disappeared. The undissolved material was removed by filtration, the solution extracted twice with ethyl acetate, the ethyl acetate layer washed once with water, then dried with sodium sulfate followed by calcium sulfate. On evaporation of the solvent 8.3 g. of red solid was obtained (D). It was dried 4 hours in a pistol at 125°C.

C. Dialysis of Substance C.

These experiments were performed by immersing a cellophane bag containing a solution of the compound in a solvent in the same or a different solvent. The whole was contained in a closed flask and the outer solvent changed at intervals. Ex. substance C (3.0 g.) was dissolved in 40 cc. absolute alcohol. A week later, it was again replaced. A total of 1.1 g. was recovered from the outer layer after one month. When the dialysis was performed in acetone 64% passed through the film. After drying four hours at 125° C. in a pistol the later material analysed as follows:

Calc. C_{31} H_{28} O_{11} $.2H_2O$		
	C 60.87	H 5.27
Found	C 60.69	H 5.01
	60.59	4.89

D. Methylation of Substance A

1. *Preparation of Methylated Substances*

X-1 to X-4

A 2 liter flask was placed on a steam bath and fitted with gas inlet, reflux condenser, two dropping funnels and glass seal stirrer. A solution of 100 g. Compound A in 400 cc. methanol was put in the flask and nitrogen gas passed over the surface during the reaction. In one dropping funnel was placed 60.3 g. (1.5 mols) sodium hydroxide (99.5%) in 100 cc. water and in the other 133 cc. (1.43 mols) dimethyl sulfate in 115 cc. methanol. Using no heat, three-quarters of each solution was allowed to run in over a one hour period. Then the steam was turned on and the mixture brought to the boiling point and the remainder of the solutions run in over a 20 minute period. The steam

was turned off and the mixture allowed to stand over-night. Water containing hydrochloric acid was then added and the precipitate filtered and washed with water. The moist solid was returned to the flask, 400 cc. of methanol added and one-fourth the previous amounts of alkali and dimethyl sulfate under nitrogen gas, followed by boiling 35 minutes under a reflux condenser. After cooling the solution was poured into water containing hydrochloric acid, the pink precipitate collected and water washed. It was then dried one hour at 109°C. The pink color appeared to deepen somewhat in light. The 107 g. obtained was dissolved in 1800 cc. absolute alcohol and 16.8 g. diazomethane in ether was added and the mixture left in the icebox two days. The precipitate was collected (71 g.) dissolved in 300 cc. benzene at room temperature, a small amount of fluocculent residue removed and the solution poured into hexane with rapid stirring, the cream colored precipitate collected, air dried, then oven dried 3 hours at 109°C. giving 56.5 g. cream colored product. The ether-alcohol solution was likewise precipitated with hexane and dried giving 21 g. more product. The materials was immersed in 700 cc. absolute alcohol for 2 hours at room temperature, the undissolved portion removed, ground in a mortar with fresh alcohol and the combined filtrates evaporated. The product (55.4 g.) was dissolved in 300 cc. benzene, a small amount of sediment removed and 2.0 g. diazomethane in ether added. After standing overnight excess ether was added, the precipitate collected, ether washed, let dry 10 minutes in air, then one hour at 109°C (45 g.) The filtrate was evaporated to 75 cc., cooled, poured into ether and the pure white precipitate (x-1) collected. It weighed 5 g. and melted at 152–3°C. The 45 g. quantity was boiled in 800 cc. absolute alcohol decanted from a small amount of undissolved material, reheated to boiling and again decanted. On cooling to room temperature a precipitate (F) formed. The filtrate was reduced in volume added to ether and 5 g. of solid (X-3), mp 173–4°C., collected. Substance F was dissolved in benzene, precipitated with ether, the precipitate dissolved in hot alcohol (700 cc.) a residue removed and the solution precipitated with ether giving 7 g. (X-4), mp. 199–200°C. The solution on standing deposited 0.9 g. more solid of mp. 197–198°C. The filtrate was reduced in volume, ether added and a further precipitate (4.5 g.) collected having a melting point of 181–3°C. (X-2).

2. *Preparation of Methylated Substances*

X-1-M TO X-4-M

A further methylation of the X products was performed by adding 1 g. of each to benzene and treating with 17 cc. of a diazomethane solution containing 2.8 g. per 100 cc. benzene. After standing three days the solutions were evaporated and the residues washed with ether.

3. *Preparation of Methylated Substance MA.*

A new methylation of substance A was carried out with certain changes. After all the dimethyl sulfate was added, the refluxing was continued for 30 minutes, the solution cooled and added to dilute hydrochloric acid. The solid was washed and kept in the dark. The second methylation was carried out with the damp solid dissolved in 400 cc. methanol and 500 cc. ethanol. 100.5 g. of pink-colored light sensitive solid was obtained. It was dissolved in 150 cc. ethanol plus 50 cc. dry benzene and 11.2 g. diazomethane in 400 cc. benzene was added and the whole let stand overnight. It was then precipitated with ether, redissolved in benzene and treated with 5.6 g. diazomethane in 200 cc. benzene, and let stand 3 days. A slight residue was removed, the solution poured into ether and the precipitate collected (58 g.). The solution on concentration gave a further precipitate (6 g.) having the highest methoxyl content encountered at anytime (31.6%). The main bulk (58 g.) contained 1.55%N. A portion was boiled in carbon bisulfide, the undissolved portion collected, and heated on a steam bath to remove solvent. It was dissolved in hot methylal. A small portion did not go into solution and was filtered out. On chilling a precipitate appeared which was collected on a filter padded with dry ice. While on the filter, it was washed with cold ether, then allowed to come to room temperature. The precipitate was again dissolved in hot methylal, an insoluble portion filtered out and the solution chilled in dry ice and acetone. The liquor was decanted and the solid redissolved in methylal. The solution was decanted from a small insoluble portion and the liquor chilled to -50°C. A precipitate appeared and it was collected on a dry ice pad and ether washed as before. It was collected and dried in a pistol five hours at 137°C. The melting point of the product was 171-2°C. with decomposition.

G. Acetylation of Substance A

1. *In The Presence of Zinc*

The following mixture was boiled fifteen minutes:

10.0 g. Substance A
60 cc. Acetic anhydride
2.0 g. Tetraethyl ammonium bromide
10.0 g. Zinc dust
1 cc. Triethylamine

The solution was decanted and the solution boiled with water to decompose the acetic anhydride. After cooling to room temperature the precipitated brown mass was collected by filtration. After dissolving in boiling methanol, it was poured into water and the resulting white precipitate filtered off and dried in a vacuum. The product weighed 12.5 g. and melted at 155-175°C. Benzene did not competely dissolve it at room temperature so the benzene

insoluble portion was filtered off. The benzene was evaporated and 10g. recovered. A second acetylation was performed by dissolving 10g. in 30cc. dimethylaniline. Acetyl chloride (10cc.) was added and the solution allowed to stand forty-six hours. On dropping slowly into excess dilute sulfuric acid, a white precipitate appeared which was collected, washed with methanol, and chilled out of solution with stirring by dry ice-acetone. The white product (8.0g.) (T) was dried in vacuo two and one-half hours at 127°C. It slightly softened at 151°C. and melted at 153–5°C.

The product is insoluble in cold alkali, but dissolves gradually in boiling alkali.

2. *In the Absence of Zinc.*

The above preparation was repeated in every detail except that the zinc dust was omitted and the benzene purification omitted. Ten grams of starting material gave 10.8g. product. The white substance softened about 162°C. but did not show a sharp melting point.

Found	C	61.48	H	4.56	Ac	45.28
		61.38		4.28		45.10

The differences from the previous compound were not significant and were in satisfactory agreement with the calculated results.

H. Deacetylation of Acetyl Derivative T

The following was refluxed for 18 hours:

1.0 g. Substance T (acetyl deriv.)
2.0 g. Potassium acetate
25 cc. Ethanol

The residue was removed and the solution poured into dilute hydrochloric acid, extracted with ethyl acetate and dried with calcium sulfate and 0.2g. deep red-brown product recovered by evaporation in vacuo on a water bath. It produced a dark color with ferric chloride and lost moisture with decomposition on being heated. The undecacetyl derivative (T) does not give a phenol test with ferric chloride.

Calc. $C_{31}H_{35}O_8(OAc)_3 \cdot 1.5H_2O$

	C 60.90	H 5.11	Ac 17.70
Found	C 60.94	H 4.85	Ac 18.70
	c 61.09	H 4.81	Ac 18.49

Roux[36] has reported that acetyl values tended to be somewhat high in his work on black wattle tannin.

I. Acetylation of the Methylated Substance (MA)

The following was boiled for fifteen minutes:

2 g. Methylated product (MA)
15 cc. Acetic anhydride
0.4 g. Tetraethyl ammonium bromide
2 g. Zinc dust
0.5 cc. Triethylamine

The solution was decanted and boiled with water. The precipitate was collected and dissolved in hot methanol. The undissolved part was removed. On chilling the solution a precipitate appeared. It was dried two hours in a pistol at 125°C. The white product melted at 163.5-165°C. and weighed 0.6 g. The entire quantity was dissolved in 10 cc. dimethylaniline and 5 cc. acethylchloride was added. After standing overnight it was dropped into excess dilute sulfuric acid with stirring. The precipitate which formed was washed with water and dissolved in hot methanol. An insoluble residue was removed and the solution chilled in ice. The resulting cream precipitate was dried two hours at 125°C. in a pistol. The product weighed 0.4 g. and melted at 174-5°C.

J. Formation Of Resorcinol In The Alkali Fusion Of Substance A.

A solution of 5 g. product A and 15 g. potassium hydroxide in 30 cc. water was heated almost to dryness in a covered pyrex dish. After cooling and taking up in water it was acidified with hydrochloric acid, extracted twice with ether, washed with water, then extracted with sodium hydroxide solution. This solution was acidified with hydrochloric acid, extracted with ether, and the ether layer dried with sodium sulfate and evaporated, giving a black tar. This was next extracted with boiling benzene, filtered, and the filtrate treated with charcoal and evaporated to a yellow-brown oil which was water soluble. The oil was dissolved in carbon tetrachloride, small back particles filtered out, the solution dried with sodium sulfate and evaporated. The resulting oil was treated with chloroform which precipitated 0.08 g. of crystals of mp. 109-110°C. The reported melting point of resorcinol is 108-110°C. It gave the fluorescein test made by heating with an equal weight of phthalic anhydride in the presence of a drop of sulfuric acid and then making alkaline. The dibenzoate was prepared by heating a few centigrams with three or four drops of benzoyl chloride in 2 cc. pyridine for a minute, then treating with water. The precipitate was washed with sodium carbonate solution and crystallised from dilute alcohol and gave a melting point of 115-116.5°C. The reported melting point is 117°C.

K. Formation Of Veratric Acid In The Permanganate Oxidation Of Methylated Substance MA.

Substance MA (5.0g.) was placed in a flask fitted with reflux condenser and dropping funnel. A solution of 30 g. potassium permanganate and 11 g. sodium hydroxide in 200cc. water was gradually run in with refluxing until no more solution was decolorised. This required 170 cc. and took two and one-half hours. The unreacted permanganate was destroyed with sodium bisulfite. The manganese dioxide was filtered out and water washed; then the filtrate was reduced in volume and acidified with hydrochloric acid liberating a large volume of carbon dioxide (identified with barium hydroxide solution). On concentration a cream precipitate appeared which weighed 0.58 g. On sublimation a pure white product was obtained leaving a very slight (1 mg.) residue. On heating, water was lost above 100°C. This was followed by resolidification and melting at 179-180°C. with sublimation. Since 1.17 g. of starting material (identified by melting point, 171-2°C.) was recovered by evaporating the acetone extract of the manganese dioxide, then 3.83 g. gave a 15 per cent weight yield of pure anhydrous veratric acid. This is a 28 per cent yield if one mole of substance MA yields two moles veratric acid.

Calc. for veratric acid $C_9H_{10}O_4$		Found
C	59.33	59.36
H	5.53	5.76
MeO	34.1	33.7
N.E.	182.17	185
MW	182.17	167.5

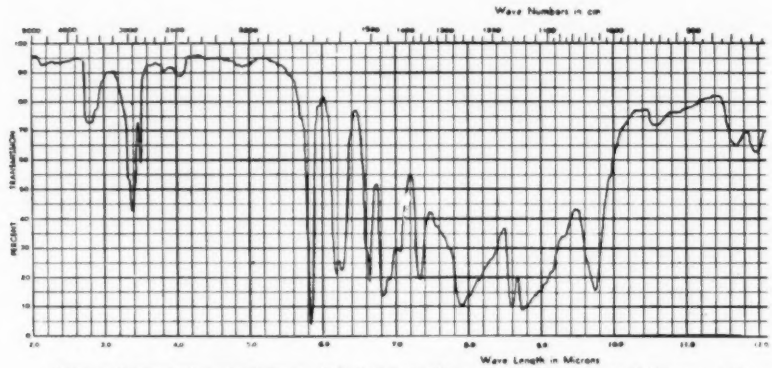
For the purpose of comparison an authentic specimen of veratric acid was prepared by oxidation of 1 part veratraldehyde by four parts potassium permanganate. The oxidation was performed at 60°C. with carbon dioxide bubbling through the aqueous solution. It was filtered hot, the liquor extracted with ether and then acidified. It was recrystallized from water. The crystals obtained melted initially at 166°C., but after solidification melted at 177°C. The lower melting point may be due to the loss of the last traces of water, but it is probably a melting point of a different crystal form and has been observed both there and with the veratric acid obtained by degradation. The low melting point does not appear after resolidification and may cause one to be deceived into believing the substance is trimethyl gallic acid which melts at 167°C.

The mixed melting point determination showed a slight softening at 173°C. The mixture was completely melted at 180°C.

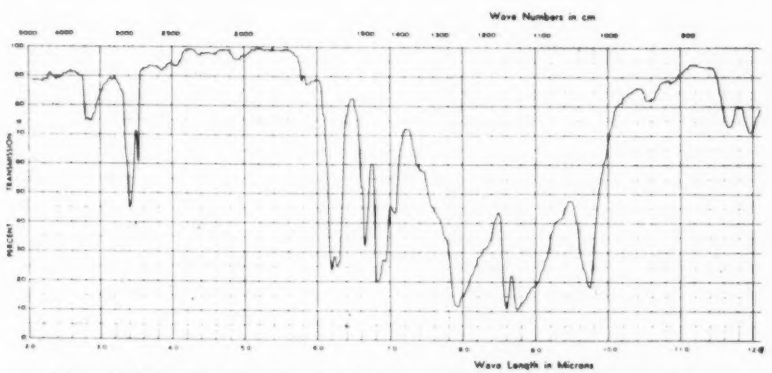
An anilide of the authentic specimen of veratric acid was made by warming the acid gently with thionyl chloride. Aniline dissolved in benzene was added and the warming continued for a minute. The mixture was treated

with water, the benzene layer then washed with dilute hydrochloric acid, then with dilute sodium hydroxide solution and finally with water. The benzene was removed on a water bath in vacuo. The residue was boiled with carbon tetrachloride and the unreacted veratric acid (identified by melting point) removed. The anilide crystallized from the solvent. The melting point was 155.5–156°C

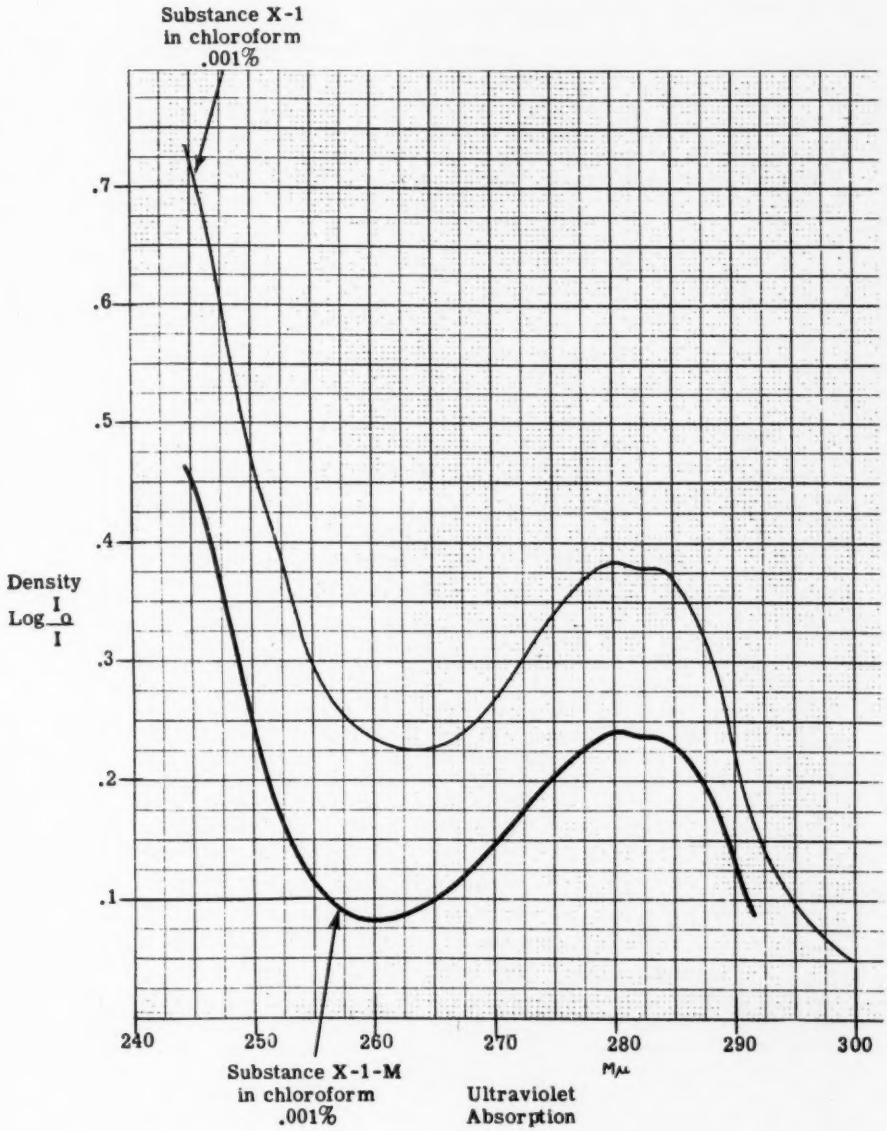
The anilide of the veratric acid obtained from the degradation was prepared in exactly the same manner. The melting point was 156–8°C. and mixed melting point 154.5–155°C.

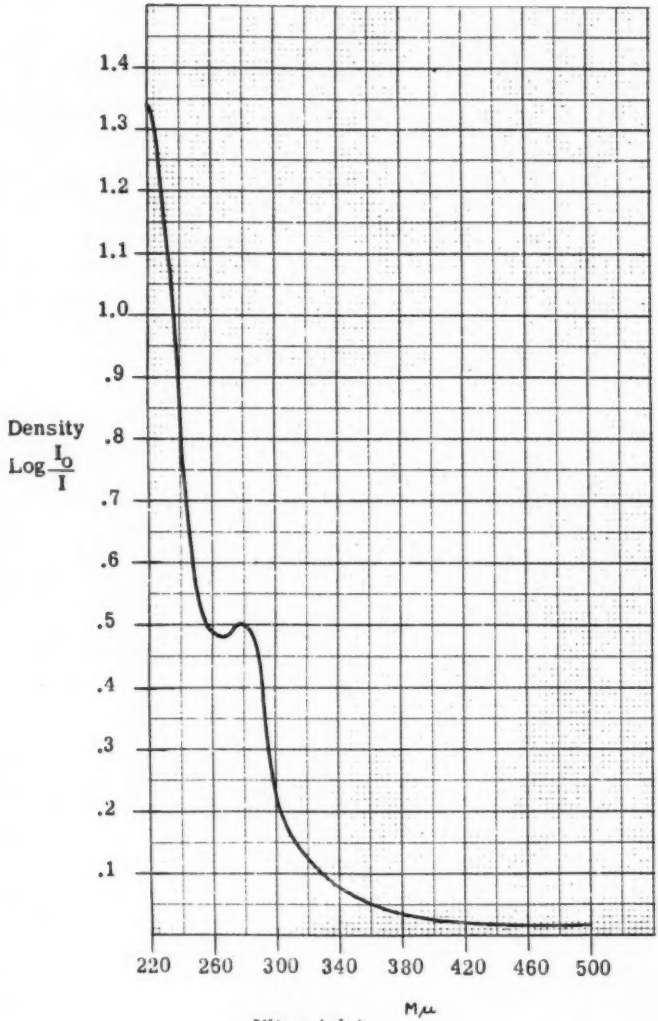


Infra-red absorption of substance X-1 (1.5 g. in 30 cc. chloroform) in an 0.25 mm. cell versus a chloroform comparison.



Infra-red absorption of substance X-1-M (1.5 g. in 25 cc. chloroform) in an 0.2 mm. cell versus a chloroform comparison.


Substance X-1
in chloroform
.001%
.7
.6
.5
.4
.3
.2
.1
Density
Log I₀/I
240
250
260
270
280
290
300
Mμ
Substance X-1-M
in chloroform
.001%
Ultraviolet
Absorption



Ultraviolet
Absorption of
Substance D
.001%
in alcohol

Bibliography

1. Rochleder, *Phytochemie*, p. 324 (1854).
2. Hlasiwetz, *Ann. Chem.* u. *Pharm.*, **143**, 290 (1867).
3. Etti, *Monatsh.*, **10**, 647 (1889).
4. Perkin et alii. *J. Chem. Soc.*, **69, 71, 73, 77.**
5. Nierenstein, *Collegium*, **146**, 69 (1905).
6. Perkin and Everest, The Natural Organic Colouring Matters, Longmans, N. Y. (1918).
7. McLaughlin and Theis, The Chemistry of Leather Manufacture, Reinhold, N. Y. (1945).
8. Freudenberg, Die Chemie der naturlischen Gerbstoffe, p. 4 Springer, Berlin, (1920).
9. Russell and Todd, *J. Chem. Soc.*, 1066, 1506, (1934); 421 (1937).
10. Pick, *Botan. Centr.*, **16**, 281 (1883).
11. Russell, *J. Chem. Soc.*, p. 218 (1934).
12. Valyashko and Rozum, *Zhur. Obshechei Khim.* (*J. Gen. Chem.*), **18**, 710 (1948).
13. Karrer and Schwab, *Helv. Chim. Acta*, **24**, 297 (1941).
14. Russell, Todd, and Wilson, *J. Chem. Soc.*, 1940 (1934).
15. Freudenberg, Karimullah and Steinbrunn, *Ann.*, **518**, 37 (1935).
16. White, *J. Soc. Leather Trades' Chemists*, **33**, 39 (1949).
17. Freudenberg and Maitland, *Ann.*, **510**, 193 (1934).
18. Shuttleworth, *J. Am. Leather Chemists' Assoc.*, **43**, 409 (1948).
19. Braunschweig, *J. Am. Leather Chemists' Assoc.*, **40**, 185 (1945).
20. Williams, *Technical Bulletin of the L.I.R.I.* No. 35 (1947).
21. Perkin and Gunnell, *J. Chem. Soc.*, **69**, 1303 (1896).
22. Jablonski and Einbeck, *Ledertech. Rundschau*, **13**, 41 (1921).
23. Einbeck and Jablonski, *Ber.*, **56**, 1906 (1923).
24. Humphreys, *J. Intern. Soc. Leather Trades' Chemists*, **18**, 178 (1934).
25. Douglas, and Humphreys, *J. Intern. Soc. Leather Trades' Chemists*, **21**, 378 (1937).
26. Compton, *J. Am. Leather Chemists' Assoc.*, **37**, 598 (1942).
27. Stather and Laufmann, *Collegium*, **816**, 164 (1938).
28. Nunez, *Anales asoc., quim Argentina*, **24**, 159 (1936) [C. A., **31**, 5339 (1937)].
29. Buchanan, Lewis and Weber, *J. Am. Leather Chemists' Assoc.*, **45**, 513 (1950).
30. Mitchell and Smith, *Aquametry*, Interscience Publ., N. Y., (1948).
31. Jarowski and Hess, *J. Am. Chem. Soc.*, **71**, 1711 (1949).
32. Clark, Semi Micro Quantitative Organic Analysis, Academic Press, N. Y. (1943).
33. Wiegand and Merkel, *Med. u. Chem.*, **4**, 585 (1942).
34. Roux, *J. Soc. Leather Trades' Chemists*, **34**, 129 (1950).
35. Perkin and Hummell, *J. Chem. Soc.*, **102**, 1460 (1912).
36. Collins, Haworth, Isarasena, Robertson, *J. Chem. Soc.*, p. 1878 (1950).
37. Seymour-Jones, *J. Intern. Soc. Leather Trades' Chemists*, **8**, 173 (1924).

Received July 9, 1951.

ABSTRACTS

The Physical Properties of Leather. Introduction; Sampling; Relative Humidity. By Gladys O. Conabere. *Chapter XIV, Part I of "Progress in Leather Science."* British Leather Mfrs. Res. Assoc., London (1948). In the U.S.A., development of official physical tests for leather has been stimulated by the tendency to include performance specifications in purchase contracts. There are few specifications of leather properties in Britain. Physical tests are valuable in research, to measure objectively the results of experiments, and in the tannery, for quality control. This chapter discusses tests found useful in B.L.M.R.A. work.

The problem of sampling has two main divisions: (1) How many hides from a lot must be tested to estimate the properties of the lot, and how should they be selected? and (2) From what position in the hide should test pieces be taken, and how many are needed? B.L.M.R.A. regards 6 sole bends as the minimum to represent a lot; they should be selected at random. The sampling position should be easily specified with reference to anatomical features. For some properties, especially tensile, direction of testing as well as position must be specified. For heavy leather, B.L.M.R.A. uses two 6-inch-square positions, one 10 inches from the root of the tail and 4 inches from the backbone, and the other a square at the shoulder-belly corner of the bend. For light leathers, samples are taken from the area just outside the flank line, toward the backbone, and in the half of the hide nearer the tail. Work by Wilson on the effect of relative humidity on physical properties is summarized. B.L.M.R.A. conditions test pieces for 3 days at 70 ± 2 per cent R.H. and $70 \pm 2°F$, as representing average conditions in Great Britain. 43 references, 3 figures.

The Physical Properties of Light Leather. By G. O. Conabere and R. H. Hall. *Chapter XIV, Part II of "Progress in Leather Science"*. British Leather Mfrs. Res. Assoc., London (1948). Important physical properties of light leather include thickness, resistance to compression, real and apparent density, strength and stretch of grain, bursting stretch, tensile strength and stretch, tearing strength, and "feel tests". Water relations will be considered in a later chapter. Thickness must be measured under slight pressure, as the surfaces of leather are not plane. B.L.M.R.A. uses a Mercer gauge (similar to Randall & Stickney gauge in U.S.A.) with a pressure of 30 g. on a foot of 1 sq. cm. area. Real and apparent densities are measured by methods used for heavy leather (see part III of this chapter). Compressibility is measured by the method of Peirce *(J. Text. Inst.* **21,** T377, 1930), with loads of 30 and 210 g. Compression modulus, h, agrees with compressibility estimated by handling. Strength and stretch of grain are measured by the Lastometer, a diaphragm tester in which load is applied to a clamped disk of leather by a ball-ended rod. For shoe upper leathers, distention at which grain crack occurs is more important than load, since leather must stretch a definite amount in lasting. With glove leather, load is more important. Glazed kid was shown to crack and burst at lower loads and distentions when relative humidity was 10 per cent than when it was 100 per cent. Mean distention per kg. of load, calculated over the first 10 kg. of load, is a useful measure of ease of stretching. Tensile strength is measured on a dumbbell specimen, 1 in. wide in the central portion, using a Goodbrand textile-testing machine, with constant rate of extension of 9/16 in. per minute. In addition to stitch-tear tests, B.L.M.R.A. uses a test in which the load required to continue a tear started by a knife cut is recorded. Tear strength does not necessarily correlate with tensile strength. "Feel" involves many physical properties that go to make up the concepts of stiffness, firmness, and compressibility. The Peirce *(loc. cit.)* Flexameter is used to measure the angle to which a horizontally clamped piece of leather will bend under its own weight. Bending length, c, defined as the cube root of the ratio of resistance to bending to the weight per unit area, is used as a measure of stiffness, and is calculated from angle of bending on the Flexometer. Flexural rigidity, G, measures resistance to bending by the fingers. It is the couple required at either end of a strip of unit width to bend it to unit curvature. Bending modulus, q, measures fullness, and takes thickness into account. It is $12G/d^3$. Other measurements of feel include temper and resilience, used by Wilson. Other tests include coefficient of friction, on which much work must be done, fineness of break, and thermal conductivity. Some typical values for light leather are given in a table. 26 references, 8 figures.

PROPERTIES OF LIGHT LEATHERS

	Density g/cc	Lastometer (grain crack) Load kg	Lastometer (grain crack) Distention mm	Lastometer (burst) Load kg	Lastometer (burst) Distention mm	Tensile str. lb/in²	Elongation at break %	Flexometer Bending length cm	Flexometer Flexural rigidity mg cm	Flexometer Bending modulus kg/cm²	Compression modulus kg/cm²	Thermal conductivity cal/cm/sec/°C
Box Calf	0.75	20	5.0	45	6.0	4,500	30	9	50,000	700	—	2.0×10^{-4}
Willow Calf	0.75	15	5.2	40	7.0	4,000	30	6	10,000	200	3.5	2.0×10^{-4}
Kid Suede	0.55	—	—	—	—	—	—	4	3,000	40	—	1.5×10^{-4}
Glazed Kid	0.65	30	6.8	50	7.8	4,000	44	5	5,000	300	2.5	1.8×10^{-4}
Dress Glove	—	10	7.0	20	—	1,500	60	2	300	10	—	—
Chamois	0.35	—	—	15	7.5	—	—	2.5	300	—	1.2	—
Roller	0.64	15	4.5	22	5.5	3,000	25	8	20,000	900	3.6	—
Hide Belly	0.82	30	6.0	50	7.0	2,800	30	—	—	—	—	2.3×10^{-4}

The Physical Properties of Heavy Leather. By R. G. Mitton. *Chapter XIV, Part III of "Progress in Leather Science"*. British Leather Mfrs. Res. Assoc., London (1948). Properties discussed include tensile strength, stretch, and other elastic properties; density; properties associated with water; thermal conductivity; and abrasion. Observed tensile strength (TS) and elongation (E) are higher for wide specimens than for narrow ones, though the difference is small for widths greater than 1/4 in. Breaking load of the full thickness of leathers is greater than the sum of the breaking loads of the splits. Increasing the rate of extension increases TS but not E. TS and E are greater at higher humidities. As the water content of untanned hide is raised, its TS passes through a maximum and then decreases, whereas that of leather continues to increase as saturation is approached. Leather breaks under tension probably by rupture of fibers, rather than slippage of fibers over one another. TS and E depend on location in the hide and direction in which specimens are cut. TS and E of heavy leathers usually lie in the ranges 3000-6000 lb/in^2 and 12-25 per cent, respectively. They differ with species of animal, buffalo hides having high TS and low E. Slow oak-bark tannage gives higher TS than rapid tannage, but prolonged tannage reduces TS. Increased water-solubles in extracts have little effect on E and breaking load, but lower TS by yielding thicker leather. If leather produced by slow tannage is loaded with solubles, TS is unaffected but E is lowered. Hot-pitting decreases TS, but bleaching has no effect. Chrome leather retanned with vegetable is stronger if the vegetable does not strike right through, and is weaker and more extensible than straight vegetable leather. Strength of curried vegetable leather is raised by increasing the fiber splitting. Heavy rolling increases TS and E. TS is increased by stretching the wet leather before drying. Currying may increase TS and E up to 15-30 per cent and 55-75 per cent, respectively. Cod oil gives greater E than mineral oil. Knowledge of TS and E is useful for belting leathers, but of little value for sole leathers.

Leather fibers follow Hooke's law. Elastic elongation $Z = aP^n$, where P is the tension and a and n are constants, the latter close to unity. For bulk leather specimens, n is about 0.7. Bulk leather elongation exceeds that of the fibers, since the configuration of the fiber network is extensible. Loose, open leathers are more extensible than tightly woven ones. Leather under repeated stress shows considerable hysteresis. The ratio of elastic extension to plastic extension may be reduced by stuffing, though the stuffing has little effect on elastic extension. For the first cycle of loading and unloading, this ratio is nearly independent of tension at which load is removed but depends on type of leather, tannage, hide location and time under stress. It increases in subsequent cycles. Factory foremen often bend leather in the hands, noting resistance to bending and tendency to elastic recovery. Similar quantitative measurements have been reported. A strip of leather may be bent into a circle in a vertical plane, supported at its lowest point; loads are added at the top and the resultant deflections measured. Strips may be tested as beams fixed at one end and loaded at the other, or as cantilevers. Such methods are difficult for heavy leather because of its inhomogeneity and the great effect of previous history of the specimen. Repeated flexing through small angles may ultimately cause grain cracking or a complete break, but it is difficult to get reproducible results. One method is to increase continually the angle of flexing throughout the test. Flexing endurance is greater for bends than for shoulders, usually varies directly with TS, and is not related to thickness or stiffness. Compression of leather changes its thickness, particularly if moisture content is high. On removal of the load there is partial recovery. Subsequent loading shows hysteresis. Heavy rolling in tanneries is equivalent to 2000-3000 lb/in^2, and residual loss in thickness is related to wear resistance of sole leather. Compression of wet leather up to 20,000 lb/in^2 has been used in estimating chemically bound water. Hardness measured by a ball-ended plunger is correlated with compressibility measured with small plates. Hardness of heavy leather is different in grain, flesh, and corium. Grain hardness is related to "firmness" and "mellowness". Corium hardness depends on relative hu-

midity and water solubles, and is related to resistance to abrasion with a coarse abradant at low loads. There is close correlation of corium hardness in wet and dry states, and compression of damp leather alters its hardness. Hardness measurements give promise of being useful in controlling pre-tanning processes.

Apparent density, d, is calculated from mass and over-all volume; real density, ρ, from mass and volume of tanned fibers. Porosity, ϵ, is $1-\frac{d}{\rho}$. Heavy leather should have low d, which results from tannery operations that give good resistance to abrasion, water resistance, etc. Over-all volume is determined either by direct measurement or immersion in mercury and measuring the upthrust or volume of mercury displaced. Apparent density varies with hide location. Heavy rolling increases d 12-15 per cent, and masks differences due to location on the hide. High density is not alone a sufficient indication of firm, compact structure suitable for shoe soles, as may result merely from heavy rolling or excessive filling. A better guide is obtained when density is measured on a specimen soaked 24 hours in water, then dried and reconditioned. A useful assessment of structure is the product of percentage hide substance and d; this product measures mass of hide substance per unit volume. Addition of water-solubles, or hot-pitting, increases d. Comparison of wet-salted and dry-salted hides shows that method of cure has no effect. Accurate measurement of p is difficult. A simple method is based on weight of the specimen in air and weight when immersed in an inert liquid, of known density, that wets the specimen; this is unsatisfactory because it requires the assumption that no solution or swelling occurs. Other methods involve gas displacement, the volume of leather and gas being measured at two different pressures, but results are not very precise. Real density is only slightly affected by type of tannage, and compression has little effect.

When heavy leather is immersed in water, absorption of water and loss of soluble matter proceed simultaneously. Both depend on surface area, volume, and temperature. In Britain specimens of full thickness are immersed in ten times their weight of water at 21°C, with edges and larger faces free to absorb, and weight gain is measured by blotting and weighing. It is customary to measure gain in weight in 15 minutes (Q_{15}) and in 24 hours (Q_{24}) as percentages of initial condition weight. Free water, F, has also proved useful; it is defined by

$$F = \frac{100(W_2 - W_3)}{W_1}$$

where W_1 is initial weight, W_2 the weight after 24 hours' immersion, and W_3 the weight after drying and reconditioning. F measures free space after removal of some soluble matter, and is little affected by subsequent soakings if the same value of W_1 is used. F and Q_{24} depend on fiber structure, and on location in the hide. Leathers with high F and Q_{24} are likely to be defective in other properties. The grain layer gives higher values, and rolling reduces Q_{15} and Q_{24}. On repeated soaking, Q_{24} approaches F. Chrome leather is more absorbent than vegetable. Filling reduces Q_{15} more than Q_{24}. Slow vegetable tannage gives values of F not much different from those obtained with rapid methods. Nature of vegetable tannin has little effect. Higher degree of tannage has little effect on Q_{15} but reduces F. Soluble material increases Q_{15} but has little effect on F. Aluminum soaps added to leather decrease water absorption. There is little relation between water absorption and rate of water penetration.

Shoe soles should have low thermal conductivity. The conductivity of leather is somewhat lower than that of rubber soling, but the difference is small. Low conductivity is associated with low apparent density. Belly soles have lower conductivity than butt portions, and heavy rolling or impregnating will increase the conductivity. Thermal conductivity rises rapidly with moisture content, and for wet leather is several times as great as for dry. The high conductivity of chrome soles as compared with vegetable is attributed to stuffing wax or

grease, since the conductivity of chrome leather free from grease is lower than that of vegetable leather.

A means of estimating the rate of wear of shoe soles would be desirable to serve as a guide for the purchaser of footwear and to assist the manufacturer in assessing the value of projected changes in his process. Actual wear tests are expensive, difficult, and time-consuming. Difficulties include variable conditions to which the soles are exposed, differences in the people wearing them, variability of leather within a bend and between bends, and the fact that loss of weight and decrease of thickness are not proportional to the time or distance for which the sole is worn. A good laboratory wear test would be very valuable. Abrasion is probably the dominant factor influencing wear. Several experiments have shown that there is a correlation between laboratory abrasion and wear in service, and the fact that a very good correlation has not yet been obtained indicates that we need a fuller understanding of abrasion testing. Such features as pressure on the abradant and abrasion of wet leather need to be studied. There is no evidence that machines which imitate the actions of walking have any advantage over those supplying a straightforward abrasive action. Choice of abrasive is difficult. Roughness and cutting power influence not only measured rates but relative rates of abrasion of different leathers. Sand is unsatisfactory because of the difficulty in standardizing particle size and shape. Abrasive stones require re-sharpening and cleaning, and it is difficult to insure that abrasive rates remain the same. The cutting power of abrasive cloth falls rapidly during the first few strokes, but quickly attains a constant value which it retains for some time if abraded material is removed. Abrasive cloth is remarkably constant within a roll and between rolls, though appreciable variations occur. Corrections for variation have been made by testing against annealed copper or rubber of known composition. Since the rate of abrasion of sole leather is much greater in the grain and flesh than in the corium, the rates of abrasion of two leathers should be compared over a considerable fraction of their whole thickness, preferably the whole thickness or a fraction that excludes grain and flesh. The rate of abrasion of a split is greater than that of the same layer tested in the unsplit condition. Rate of abrasion is low in the butt, high in the shoulder and belly edge. Variations over a bend relate to differences in fiber structure, and estimates of rate of abrasion can be based on microscopic examination. Hard leathers have low rates of abrasion. Temperature has little effect, but low humidity increases rate of abrasion. Pre-conditioning before test is practically without effect. Rate of abrasion increases rapidly as applied load is raised. At low loads abrasive particles apparently cut fibers, while at high loads they are torn from the surface. Direction of abrasion is relatively unimportant. Rate of abrasion is a maximum for an intermediate grade of abrasive, lower for coarse or fine grades. Rate may be calculated as loss of thickness or volume, if the load is not high enough to compress soft leathers, or as loss of weight, which may give a ranking of samples different from that given by loss of thickness, as densities vary, particularly when effects of treatments that alter density are studied. Energy required to abrade away a given volume may also be used. All three types of measurements give generally similar results. The results of wear tests in service may be expressed as hours wear per unit loss in thickness, or different leathers may be compared as to rate of loss of thickness or change of other quantities such as thickness/density, thickness/hide substance, etc.

If opposite sides of a hide are tanned with chrome and vegetable respectively, the chrome leather is thinner but more durable. Chrome soles are more slippery in wet weather, lose their shape, and are very permeable to water unless impregnated. Chrome-vegetable retan soles have somewhat the same advantages and disadvantages. There is little evidence that modern rapid tannages give less durable leather than that produced by slow tannage, and some trials have indicated that modern tannages are more durable. Excessive water-solubles decrease rate of abrasion and wear in service. Very low hide substance is unsatisfactory, but above a certain limit a low value does not necessarily result in poor wear. Hot-pitting and

bleaching have little effect on wear. Wet-salted and dried hides give similar results. Leathers made from fresh hides are superior to those from salted ones. Ageing of some finished leathers improves abrasion resistance, but is without effect on others. Glucose and Epsom salts make little difference. Impregnation with oils, waxes, etc. has been shown to improve durability of American leathers somewhat, but it is doubtful that British leathers would benefit from such treatment. Abrasion tests on impregnated leathers are often misleading because of clogging of the abrasive. Heavily rolled American leather shows a slight improvement over unrolled leather in wear and abrasion tests. British leathers are not improved by compression. Rolling may be deleterious if water-solubles content is low. Little is known about the abrasion of wet leather. 205 references. R. B. H.

The Warble Fly and a Plan for Combatting It. By J. A. Sagoschen and F. Weiler. *Oesterr. Leder-Zeitung*, **6,** 66, 88 (1951). A review is given of the biology of the warble fly and of Austrian regulations for its control. There are five possible ways of exterminating the warble: (1) destroy the flies, (2) prevent laying of eggs, (3) destroy the eggs, (4) destroy the pupa, (5) destroy the larvae. Up to the present, only mechanical removal of the grubs or treatment with derris preparations have any prospect of success. Large scale practical tests are proposed of the two following methods: (a) use of a chemical preparation that will attract then kill the flies, and (b) use of a chemical that will repel the flies and so prevent them from laying eggs. I. D. C.

Drives for Tanning Drums. By W. Thomas. *Das Leder*, **2,** 151 (1951). The types of drives in commercial use for tanning drums are described, in particular that made by A. Fried, Flender & Co. If the drum is used for several purposes, it may require a drive that will vary the speed continuously. In general, a fixed speed between 4 and 14 revolutions per minute is sufficient. The drive should automatically reverse the direction of drum rotation after a certain number of revolutions. I. D. C.

Astringency Problems with Water Soluble Organic Tanning Materials. III. The Influence of Hydrotropic and Buffering Nontannins on the Purity Curves of Novolaksulfonic Acids. By A. Küntzel and H. Grunewald. *Das Leder*, **2,** 127 (1951). Purity curves for novolaksulfonic acid (a phenol formaldehyde condensation product prepared as described in Part I; *(this Jour.*, **46,** 387) where obtained at pH 3.6 after the following modifications: (a) adjusting to pH 3.6 with sodium hydroxide (unbuffered), (b) adjusting first to pH 7 with sodium hydroxide and then to pH 3.6 with acetic acid, (c) adjusting to pH 3.6 with sodium hydroxide, then adding acetate buffer to give an acetate ion concentration of 0.1 mole per liter, (d) as "c", except that the acetate ion was increased proportional to the tannin concentration. Weakly chromed Freiberger hide powder was used for the analyses. The curve for the unbuffered solution was typical for this type of syntan; purity rose to a maximum of 70 or 80 at a concentration of 2 or 3 grams of dry matter per liter, then gradually dropped to approximately 50 at a concentration of 12 or 13 grams per liter. The curves for the other solutions resembled those for natural tannins in that they rose to a maximum of approximately 60 at a concentration of 2-4 grams per liter, then remained nearly constant as concentration increased further. The curves for the other solutions resembled those for natural tannins. Buffering is therefore a possible explanation for the different types of curves found for commercial syntans. In the previous article it was shown that the sharp decrease in purity as the concentration of the analytical solution was increased, was due to the presence of over-sulfonated fractions (semitannins). The increase in fixation of these semitannins caused by the presence of acetate may be explained in two ways. Acetate

may stabilize the pH and so maintain the supply of free sulfonic acid from the neutral salt; the free acid is readily taken up by hide powder, whereas the neutral salt has a low astringency. The second possibility is that the acetate acid in the buffer peptizes the collagen making it more absorptive. Acetic acid has a different type of swelling action on collagen from mineral acids. An excess of acetate acid does not repress swelling as does an excess of hydrochloric or sulfuric acid. At higher concentrations the undissociated acetic acid causes hydrotropic swelling which is greater, the greater the concentration of acid. As concentration increases, the original ionic acid swelling changes over smoothly to hydrotrope swelling and finally to gelatinization of the collagen. When N/10 acetate buffer is passed through an analytical filter tube of hide powder it dissolves much more hide powder than water. Not only are fine particles dissolved by the buffer solution, but the large insoluble portion of the hide powder is swollen, so that large tannin particles can penetrate and combine with the hide. In other words, the surface of the insoluble main portion of the hide powder is modified toward gelatine, so that it fixes semitannins. To further investigate the role of peptization, analogous experiments were made with ammonium thiocyanate and urea, two nonbuffering, hydrotropic swelling agents. Urea, which has only slight peptizing action, gave a curve similar to that for unbuffered syntan. The curve with thiocyanate was similar to those for vegetable tannins, so that peptization is an explanation for the difference in curves. On heavy hides acetate-buffered sulfonic acid produced good leather, whereas unbuffered syntan or that containing thiocyanate produced only very poor, cracky leather. Perhaps the peptizing action of thiocyanate is too vigorous. A sulfonated Novolak containing a large amount of phenolsulphonic acid gives a flatter purity curve (resembling that for vegetable tannin) than Novolaksulfonic acid made by sulfonating a phenol-free, dry Novolak. The phenolsulfonic acid acts as a hydrotropic swelling agent and so improves the absorptive power of the hide powder for tannins of low astringency. However, the tanning action of the former syntan (containing phenolsulfonic acid) is poor compared to the latter, because it must be more highly sulfonated to make it soluble. Vegetable tannins contain fractions having hydrotropic action, similar to that of acetate; part are phenolic nontannins and part are tannins of low molecular weight. The removal, by washing, of these substances having hydrotropic action raises shrinkage temperature, but lowers leather quality.

Astringency of a tannin system resides not only in the properties of the tannin particles (size, acid or phenolic character), but also in the accompanying substances, either definite nontannins or intermediate substances, such as phenolic nontannins, low molecular weight tannins, semitannins, etc. The complex conception of astringency is related not to the tannin as a chemical individual, but to the whole tanning system. The nature of this system depends not only on the method of preparation, but it can be altered easily by the tanner by addition of acid, buffers, wetting agents, etc. I. D. C.

A Reaction for Identifying Organic Masking Agents in Chrome Tan Liquors. By J. Plapper. *Das Leder*, **2**, 78 (1951). Starting with the known method for detecting phthalic acid by fusion with resorcin and sulfuric acid to produce a green fluorescence, it was found that mono- and di-basic aliphatic and aromatic carboxylic acids and aldehydes would react in the same manner. The reactions require a reactive C-O group to permit condensation to a 6-hydroxylfluorone derivative. This group is present in anhydride forming carboxylic acids and aldehydes but not in ketones. The latter do not normally produce fluorescent compounds, but if the reaction mixture is heated above 150°, carbon monoxide may be liberated and fluorescent dyes formed. The presence of masking agents in chrome tan liquors can be detected by the resorcin-sulfuric acid reaction and the agent can be identified provided it is a single salt and not a mixture.

The method is as follows: To an amount of solid or liquid chrome liquor containing approximately 0.25 grams Cr_2O_3, add sufficient sodium hydroxide to redissolve the chromium

as chromite, boil a short time and filter off the chromium hydroxide. Neutralize the filtrate with sulfuric acid and evaporate to dryness. Treat the residue in a test tube with 0.1 gram of resorcin and 1 cc. concentrated sulfuric acid, then heat over a small flame to 190-200°C. When this temperature is reached, pour at once into 400 cc. of water in a 600 cc. beaker, stir and make slightly alkaline with sodium hydroxide. Fluorescence indicates the presence of masking agents.

For identifying the common masking agents note the following: (1) color changes and behavior of the mixture during heating,—if gas is formed determine whether it is carbon monoxide, carbon dioxide or both; (2) color of the solution in the 400 cc. of water; (3) color and fluorescence of the alkaline solution; (4) observe colors and fluorescence by daylight or light from a daylight bulb. To obtain more intense colors, prepare another tube as above, but when the temperature reaches 190-200°C hold it at this temperature for one minute or for two minutes. The behavior of various salts during heating with resorcin and acid is as follows:

Formate—pink before heating, then orange changing to bright green; CO evolved.
Acetate—little reactive, faint yellow, yellow-green.
Oxalate—blue-blue-violet, when warm; fades on heating with formation of CO and CO_2 and color becomes yellow-green.
Phthalate—no gas; color change, intense yellow, orange, yellow-green.
Malonate—CO_2 is formed, otherwise like acetate.
Succinate—no gas; yellow, orange, yellow-green.
Adipate—no gas; yellow-green, red-brown, dark brown.
Tartrate—CO formed on gentle heating; color fuchsin-red at once then dark red.
Glucose reduced liquor—slight gas formation, mainly CO_2; intensive yellow, red, dark red, red-brown.
Formaldehyde—dark red before warming.

After dilution the following colors are formed:

Salt	*Acid Solution*	*Alkaline Solution*	
		Color	*Fluorescence*
Formate	faint yellow-green	faint pink	bright green
Acetate	colorless	colorless	faint dark green
Oxalate	colorless	colorless	faint dark green
Phthalate	strong yellow	faint red-brown	strong yellow-green
Succinate	yellow green	faint pink	Olive green
Adipate	strong yellow-green	fuchsin-red	blue-violet green
Tartrate	colorless	orange	
Glucose	faint yellow-brown	red-brown	olive green
Formaldehyde	red-brown	dark red	dark green

I. D. C.

Separate and Combined Deliming and Bating. By O. Grim. *Das Leder*, **2**, 73 (1951). The deliming and bating of skins for various types of leather are described in detail. Bating should loosen and remove the epidermis, noncollagenous protein, the walls of fat and sweat glands, fibroblasts, lime soaps and fats. Elastin removal is not the important function. Separation of the operations of deliming and bating has the appeal that it separates two processes having different reaction rates and that are each difficult to control, but it requires more time than the combined process. Also it is very troublesome, especially in a factory working heavy hides, if all the lime must first be washed from the hides and then they must be

treated for several hours in an enzyme bath. As a rule, enough lime should be carried over into the bate to adjust the pH to 8.5–9.0, the optimum for bating, but too much must not be carried over or it will not be removed in the bating process.

The combined process has the disadvantages that enzyme action does not start until deliming has lowered the pH to near the optimum; thin parts of the skin are delimed and bated first; thick parts of the skin are delimed and bated on the surface, but not in the center until near the end of the process. For deliming, acid of some type is needed. The cheapest acid is hydrochloric, but it causes swelling of the skin and produces calcium chloride, which peptizes the skin. Sulfuric acid produces calcium sulfate, which has a solubility of only 0.2 per cent, so that a large float is needed. Formic, lactic, acetic and butyric acids all cause swelling before deliming is complete. Boric acid does not cause swelling but removes lime only in the capillary spaces. Ammonium chloride produces calcium chloride and also produces loose flanks. Ammonium sulfate removes the lime as calcium sulfate which has a low solubility. A suitable process for large factories is to use a bate containing ammonium salts, to add acid or an acid deliming agent to keep the pH at 7 until the desired deliming is attained, then to complete the bating at pH 8.5–9.0. I. D. C.

Introduction to the Fluorescence Microscopy of Tanning Materials. By Franz Dangl. *Oesterr. Leder-Zeitung*, **5**, 60, 78, 129, 168 (1950). The physics of light is reviewed. Specifications are given for various types of lamps used as light sources. (Future installments are to describe methods.) I. D. C.

Formulas for Calculating the Amounts of Acid, Base or Masking Agents to Add to Chrome Liquors in Order to Change the Basicity or Degree of Masking. By J. Plapper. *Das Leder*, **2**, 29 (1951). The amount of chemical, in grams per liter, to be added to a chrome liquor to change the basicity by a given amount, B (in per cent Schorlemmer), is given by the formula C B F, where C is grams of chromic oxide (Cr_2O_3) per liter and F is a factor. The formula C M F gives the grams per liter of masking salt to be added to obtain the percentage of masking, M. The following factors, for pure materials are given. For commercial chemicals the factor should be increased by dividing by the purity of the material.

Hydrochloric acid, HCl	.01439
Sulfuric acid, H_2SO_4	.01936
Oxalic acid, $H_2C_2O_4$	.01777
Formic acid, HCOOH	.01817
Soda ash, Na_2CO_3	.02092
Sodium formate, HCOONa	.02684
Sodium oxalate $Na_2C_2O_4$	.02645
Sodium metabisulfite $Na_2S_2O_5$	.01876
Sodium sulfite Na_2SO_3	.02487
Sodium adipate, $Na_2C_6H_8O_4$	.03752
Sodium phthalate, $Na_2C_8H_4O_4$	.04146

Examples:

1. How much sodium carbonate is needed to bring 300 kilograms of zero-basic chrome alum containing 15 per cent Cr_2O_3 to a basicity of 33 per cent?

45 x 33 x .02092 = 31.07 kilograms of pure sodium carbonate.

45 x 33 x .05654 = 83.96 kilograms of crystalline sodium carbonate (37 percent).

2. A chrome liquor containing 120 grams of Cr_2O_3 per liter and having a basicity of 45 per cent is to be brought to a basicity of 25 per cent. How much 37 per cent hydrochloric acid is required per liter of liquor?

[Factor = .01439/.37 = .0389]

120 x 20 x .0389 = 93.36 grams.

3. How much sodium formate is required to mask a chrome liquor containing 140 grams Cr_2O_3 per liter to a degree of 8 (to mask 8 per cent of the chrome)?

140 x 8 x .02684 = 30.06 grams per liter. I. D. C.

Classification of Surface Active Compounds. By Ernst Götte. *Das Leder*, **2**, 102 (1951). The following classification of the surface active agents important for the tanning industry is proposed:

A. Ion forming compounds
- I. Anion active compounds
  - 1. Soaps
  - 2. Alkyl sulfates
    - (a) primary
    - (b) secondary
    - (c) with free or blocked carboxyl groups
  - 3. Alkylsulfonates
    - (a) primary
    - (b) secondary
    - (c) with blocked carboxyl groups
    - (d) alkyl-aryl sulfonates
- II. Cation active compounds
  - 1. Amino salts
  - 2. Quaternary salts
- III. Ampholitic compounds

B. Nonionic surface active compounds
- I. Ethylene oxide condensates
- II. Albumin condensates. I. D. C.

New Developments in the Opaque Coating Field. By K. Eitel. *Das Leder*, **2**, 49 (1951). A review of recent work on leather coatings, much of it from English and American sources. I. D. C.

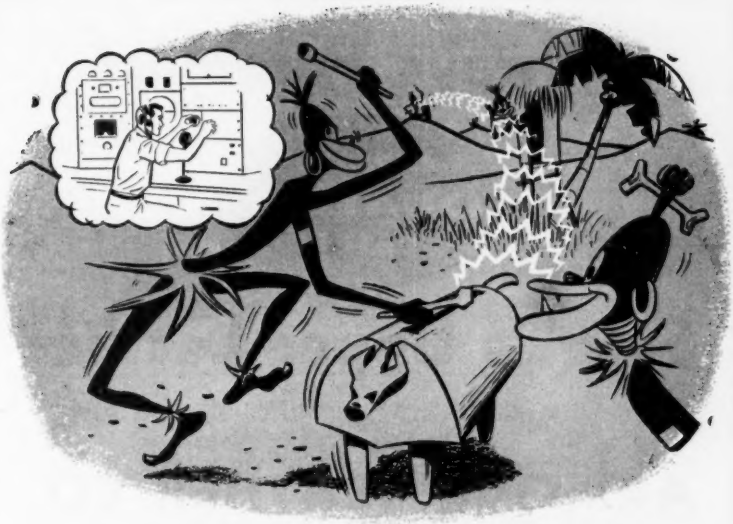
Dust Hazards in the Leather Industry. By Walter H. Geck and Th. Windel. *Das Leder*, **2**, 57 (1951). A general discussion is given of dust hazards and dust disposal problems. A survey of the industry showed that dust explosions were unknown, but that nearly all firms had had dust fires. The causes of the fires were usually unknown, but high fat content of the leather favored fires. Various means were used for collecting or disposing of the dust. Danger points are bark storage and grinding and dust collectors from buffing and brushing machines. Types of dust that endanger the life and health of employees are rare or absent in the leather industry. I. D. C.

The Use of the "Phosphate-Inoculation-Process" in Leather Manufacture. By C. Riess. *Das Leder*, **2**, 125 (1951). The use of sodium hexametaphosphate (calgon) in the "threshold treatment" of water to prevent precipitation of calcium carbonate is reviewed. The process also retards oxidation and precipitation of iron. A commercial (German) apparatus for introducing from 2 to 5 grams of metaphosphate per cubic meter of water is illustrated. I. D. C.

Dependence of the Shrinkage Temperature of Vegetable Tanned Collagen on Degree of Tannage. By A. H. Gustavson and Magne Nestvold. *Das Leder*, **2**, 121 (1951). To study the relation between degree of tannage and shrinkage temperature, laboratory tanned pieces of calfskin were used. The raw skin had been well delimed, dehydrated with acetone, then air dried. It had a shrinkage temperature of 64°C when measured on strips suspended by one end, and 68° when measured in a shrinkage temperature apparatus.

The tanning materials were acetone solutions of (1) quebracho extract containing 23 grams of tannin and 3 grams of nontannin per 100 milliliters and (2) mimosa extract containing 17 grams of tannin and 2 grams of nontannin per 100 milliliters. Three-gram portions of skin were treated with from 1 to 12 milliliter portions of the tannin solution for 24 hours after which they were transferred to 20 cc. of water for 24 hours. Shrinkage temperature increased as degree of tannage increased to 30 or 35, then remained more or less constant with further increase in degree of tannage. Tannin absorbed after the degree of tannage reaches 30 does not contribute to the shrinkage stability of the protein lattice. When hide powder was treated with sulfo acids to completely block the basic groups, absorption of tannin was reduced from 30 per cent (based on the weight of protein) to 5 per cent. The tannin that is first taken up by collagen and that gives collagen its shrinkage stability, therefore is attached to basic groups.

Soluble matter lowers shrinkage temperatures. Leather tanned 14 days at pH 3 with myrobalans contained 63 grams of total and 28 grams of combined tannin per 100 grams of collagen. It had a shrinkage temperature of 60°C but this was raised to 68°C by washing out all uncombined tannin. The shrinkage temperature of similar leather tanned at pH 5 was raised from 67° to 74° by washing. I. D. C.



NOTHING LIKE IMPROVEMENT!

...and the "Double Action" New NOPCOLENES bring you improvement PLUS

When Bongo and his brethren relayed a message fifty miles within minutes, by whamming log drums, they thought their ambidextrous performance spelled the "last word" in long range communication. But today's two-way radio handles the distance in split seconds. A fine example of improved "double action" if ever there was one!

And it's much the same with Nopcolenes. We reckoned we had sound reasons for believing our initial "double action" Nopcolene* fatliquors provided the most important means ever devised for making good leather better—but when we put them to work, and checked closely, we discovered how to make them still more efficient.

Today, our *improved* Nopcolenes are truly unique. Their sensational "double action" characteristic affords *superb surface lubrication plus easily-controlled penetration.* Used singly or in combination, they enable the tanner to obtain leather with *any* degree of surface feel, temper, hand, break and stretch desired.

Send for full information.

Free! This new book gives up-to-the-minute data about Nopco's *improved* Nopcolenes, and formulas for various leathers. Make sure you send for your copy now.

NOPCO TRADEMARK EVOLVED THRU RESEARCH

Nopco Oils Make Good Leather Better

NOPCO CHEMICAL COMPANY, Harrison, N. J.

Branches: Boston • Chicago • Cedartown, Ga. • Richmond, Calif.

*T. M. Reg. U. S. Pat. Off.

Always Foremost

Armour's QUALITY Leathers USA

Sole and Upper Leather

•

ARMOUR LEATHER CO.

Chicago Boston New York

KOREON

MUTUAL CHEMICAL CO. OF AMERICA — MUTUAL — SINCE 1845 — NEW YORK, N.Y. — REG. U.S. PAT. OFF.

MUTUAL'S PREPARED ONE-BATH CHROME TAN

Sodium Bichromate - Potassium Bichromate

Mutual Chemical Co. of America

270 Madison Avenue New York 16, N. Y.

Plants: Jersey City, N. J. — Baltimore, Maryland

UNION TANNERS SUGAR CHIPPED OR BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR
CHIPPED OR BILLETS UNION TANNERS SUGAR
NO NG
UN ETS
UN AR
CH AR
NON-FOAMING UNIFORM CLEAR NON-FOAMING
UNION TANNERS SUGAR CHIPPED OR BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR

UNION STARCH & REFINING CO.
Established 1903
General Offices: COLUMBUS, INDIANA

THE LEATHER MANUFACTURER
ESTABLISHED 1883

Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

Affords complete tannery coverage, concentrated among tanners, chemists and buyers of materials, raw stock and equipment.

Technical articles and newsworthy features invited for publication.

THE LEATHER MANUFACTURER
NEW YORK OFFICE
171 William St.
BOSTON OFFICE
683 Atlantic Ave.

CALAFENE
Binder and Filler

PIGMENT FINISHES Uniform quality binder, filler and carrying agent. Builds up body. Improves covering power and spread. Nourishes fiber and eliminates harsh feel. No manipulation necessary.

LEATHER FILLER Imparts permanent flexibility. Does not "pipe" or crack. Covers cuts and imperfections.

SUEDE SPLITS Plumps the skins, strengthens and builds up low ends. When sueded the skins have a velvety nap and full mellow feel. Does not lay on the surface.

APEX
MARK of QUALITY

Established 1900
Apex Chemical Co., Inc.
225 West 34th St., New York 1, N. Y.

Manufacturers of a complete line of specialties for the tanning trade

HOWES LEATHER CO. INC.

SOLE LEATHER

•

Tanners Cut Sole Division

•

CUT SOLES

BOSTON, MASS.
ST. LOUIS, MO CHICAGO, ILL.

BONA ALLEN, INC.

Buford, Georgia

TANNERS SINCE 1873

•

Finest English Rein and Strap Leather

Latigotan Harness Leather

Manufacturers of genuine English type and full rigged hand tooled roping saddles.

Warner

BELL-MINE LIME

Year-round Uniformity
Dependable Source of Supply

WARNER COMPANY

Bellefonte Division, Bellefonte, Pa.

PITTSBURGH - - - - PHILADELPHIA - - - - NEW YORK

THE OHIO LEATHER CO.

LUXOR CALF COLORS **BLACK JETTA CALF**
WASHETTE • WHITE AND COLORS

TANNERY & GENERAL OFFICES: GIRARD, OHIO
BOSTON • NEW YORK • ST. LOUIS • CHICAGO

EISENDRATH FINE CALF LEATHERS

IN COLORS AND BLACK

B. D. Eisendrath Tanning Company

801 Merchandise Mart, Chicago, Ill. • Tannery at Racine, Wisconsin

195 South St., Boston, Mass., Day Gormley Leather Co. 12 E. 33rd St., New York City, Moe Shapiro

TANIMEX CORPORATION

39 BROADWAY **NEW YORK 6, N. Y.**

SOLE AGENTS FOR NORTH AMERICA

ORDINARY SOLID QUEBRACHO EXTRACT
CLARIFIED SOLID QUEBRACHO EXTRACT

Produced in Paraguay by:

Carlos Casado Limitada
Campos y Quebrachales Puerto Sastre S. A.
Sociedad Forestal de Puerto Guarani S. A.

. . . .

SOLID WATTLE EXTRACT - H.E.C. BRAND

Produced in South Africa by:

Hodgson Extract Co., Limited

. . . .

SPRAY DRIED TANNING POWDERS

Of extraordinarily high tannin concentration - completely and immediately soluble in cold water - ideal for drum tannage

QUEBRACHO MYROBALAN
MIMOSA VALONEA

Produced in England by:

Richard Hodgson & Sons Limited

. . . . . .

REILLY-
WHITEMAN-
WALTON CO.

OILS of CHARACTER

CONSHOHOCKEN, PA.

BORAX · BORIC ACID

Borax and Boric Acid have long been used as chemicals in the tanning and finishing of good leather.

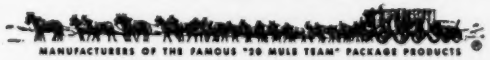
Distributors of Pacific Coast Borax Co. are located in principal cities of the United States

Write for our Booklet: "Processing Heavy Leather"

PACIFIC COAST BORAX CO.

Division of Borax Consolidated, Limited

LOS ANGELES • NEW YORK • CHICAGO • CLEVELAND



MANUFACTURERS OF THE FAMOUS "20 MULE TEAM" PACKAGE PRODUCTS

Where Coverage Counts!

Shoe and Leather REPORTER

TANNERY BUYER

THE TECHNICAL JOURNAL FOR SUPERINTENDENTS, CHEMISTS, TANNERS AND BUYERS

Now more popular than ever! **Shoe and Leather Reporter's** TANNERY BUYER Section, published in the third issue of every month, is read by every important executive, superintendent, chemist, and buyer. It has coverage where coverage counts!

Shoe and Leather
REPORTER
Representatives in

Boston (Hdqtrs) — Washington
Chicago — St. Louis
New York — London, Eng.
Philadelphia — Los Angeles
San Francisco

SHOE AND LEATHER REPORTER
210 Lincoln Street, Boston, Mass.

Salem Oil & Grease Co.

FAT LIQUORS

FEATURING

CONTROLLED PENETRATION

●

SALEM, MASSACHUSETTS

STANDARD HIDE POWDER

A material made to specifications and used internationally for the analysis of vegetable tanning materials

Hide Powder Division
of the
KEYSTONE TANNING AND GLUE COMPANY
RIDGWAY · PENNSYLVANIA

Tanners Use Clinton's special prepared, laboratory tested products to assure unvarying uniformity.
CORN SUGAR • CORN STARCH • CORN SYRUP • LACTIC ACID
Over 44 years experience behind Clinton's laboratory service to tanners.
CLINTON FOODS INC.
CLINTON, IOWA
CLINTON

KEPECO FINNALINE KEPOLAC
EMULLO FRESKO FONDO
RICCOTAN UNI-LAK
(Reg. U. S. Pat. Office)

KEPEC CHEMICAL CORPORATION
Milwaukee 1, Wisconsin

ARTHUR C. TRASK CO.
Tanners Oils & Extracts
CHICAGO, ILL.
4103 S. LASALLE ST.

..... LET'S GET THE ANSWERS ABOUT MAGAZINE LEADERSHIP *in the Tanning Industry...*

Which magazine does the outstanding job in editorial service?
Which magazine has 87% more paid and audited circulation?
Which magazine carries more than 100% more advertising?

Tanning industry executives know that only in Leather and Shoes do they get the complete and timely job in news, markets, features, and editorial service.

Complete and often *exclusive* coverage of technological progress in tanning methods and production, supplies, materials, equipment and machinery, *plus* the facts about demand, markets, uses, and trends in the leather-using division of the industry, *plus* the keenest, most thought-provoking editorials on the leading problems and interests of the entire field.

Because they get the fullest measure of service each week, tanning executives subscribe to L & S at an 87% higher rate than to the second paper —almost 2 to 1 leadership.

This leads naturally to greater productivity for advertisers who respond with the greatest volume of advertising. L & S carries 124% more tanning material, chemical, oil, etc., advertising than the second paper, and 117% more tanning machinery and supply advertising.

That's the story about magazine leadership in the tanning industry. It's L & S all the way. If you want more facts, write us today.

L&S

LEATHER AND SHOES
300 W. ADAMS STREET
CHICAGO 6, ILLINOIS

Finishes
for all types of
Leather

FINE LEATHER FINISHES
NLF

NEWARK
LEATHER FINISH CO.
8 WILHELM ST. HARRISON, N. J.
Telephone: Humboldt 5-3470

MORITE BRAND
EST. 1908

MORITE BRAND
Sulphonated and Compounded
OILS

MORITE BRAND
EST. 1908

WHITTEMORE-WRIGHT COMPANY, INC.
62 ALFORD ST. CHARLESTOWN DISTRICT BOSTON, MASS.

FOR VEGETABLE TANNED SOLE LEATHER

THE BEST
BESCO
COMPOUNDS

FOR CHROME CHROME RETAN SOLE LEATHER

TANNERS' SUGAR **LACTIC ACID**
BUFFALO EXTRACT & SUPPLY CO. ·:· BUFFALO, N. Y.

Look to the Leader...

CALCO

Dyes for Leather

Continuous research for new product development and improvement makes Calco a leading supplier of top quality dyes for leather.

Whatever your requirements in leather coloring, consult your Calco representative... and be assured of expert technical assistance to guide your selection of the *right* dyes for the job.

Calco®

AMERICAN Cyanamid COMPANY

CALCO CHEMICAL DIVISION, DYESTUFF DEPARTMENT

BOUND BROOK, NEW JERSEY

NEW YORK, CHICAGO, BOSTON, PHILADELPHIA, CHARLOTTE, PROVIDENCE

REPRESENTED IN CANADA BY NORTH AMERICAN CYANAMID LIMITED, CALCO CHEMICAL DIVISION

MONTREAL—TORONTO

*HABU-COAT *Tannery Finishes Supreme*

*LABORATORY CONTROLLED AND TESTED

as developed by **HADLEY'S**

...for ANILINE, SEMI-ANILINE *and* PIGMENTED EFFECTS...

...GIVE "CHARACTER" and "FEEL" to YOUR LEATHERS

These new formulations... available in any color range... are made to your specific requirements for all type leathers. Quality control is assured by strict laboratory pre-testing. HABU-COAT Tannery Finishes represent a marked achievement in the development of "effects" that give "character" and "feel" to all your leathers. What are your needs?

IN ALL THE POPULAR COLORS

for SHOE • GARMENT • GLOVE • LUGGAGE • UPHOLSTERY

SEE YOUR NEAREST REPRESENTATIVE OR WRITE US DIRECT

•

IN MILWAUKEE
William Barry
935 N. 35th St. • WEst 3-3344

SINCE 1919
HADLEY BROS.-UHL *Company*
514 CALVARY AVE. • ST. LOUIS 15, MO.

TYPICAL ANALYSIS OF BARIUM'S

SODIUM SULPHIDE FLAKES

Fe	0.0005%
Other Heavy Metals	Nil
Na Cl	0.40
Other Na_2O (not oxidizable)	1.35
Na_2S	61.00

Manufactured in large tonnages by

BARIUM REDUCTION CORPORATION

SOUTH CHARLESTON 3, WEST VIRGINIA

need we say more?

AIXXX

Barkey Importing Co. Inc.

44 East 53 St., New York 22, N. Y.

IMPORTERS

Vegetable Tanning Extracts

and Raw Materials

Wattle Bark

Wattle Extract

Quebracho Extract

Valonia Cups, Beards

Valonia Extract, Valex Brand

Mangrove Bark

Sicily Sumac

Myrabolans

Divi divi

SOLE AGENTS FOR UNITED STATES AND CANADA

for

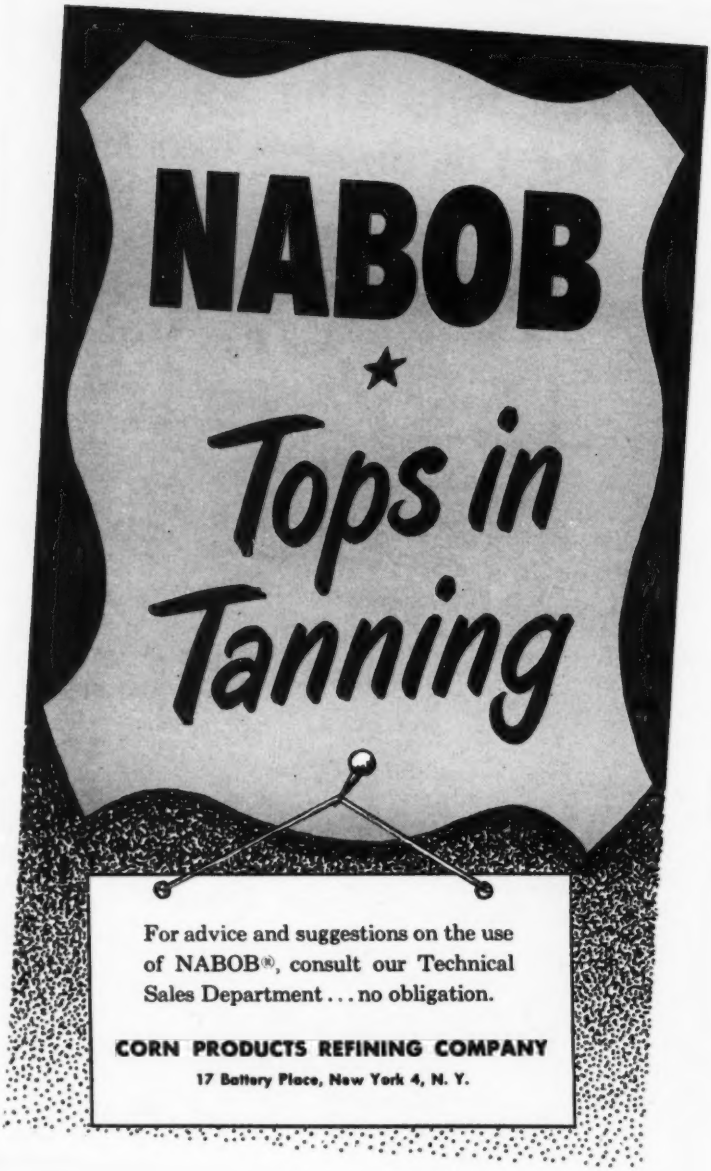
Italian Chestnut Extracts

Solid and Powdered

Produced by

S. A. LEDOGA

MILANO, ITALY


NABOB
★
Tops in
Tanning
For advice and suggestions on the use of NABOB®, consult our Technical Sales Department . . . no obligation.
CORN PRODUCTS REFINING COMPANY
17 Battery Place, New York 4, N. Y.

THE TANNERS' COUNCIL RESEARCH LABORATORY

at

THE UNIVERSITY OF CINCINNATI

is

THE DEPARTMENT OF BASIC SCIENCE

in

THE GRADUATE SCHOOL OF ARTS AND SCIENCE

The purpose of the laboratory is to conduct scientific research in the fields of Science concerned with Tanning and Leather.

To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.

"The Extension of Knowledge is by the Investigation of Matter".

This space dedicated to
Tanners' Council Research Laboratory
by a Friend

FATLIQUORS

For every type of leather

Manufactured by

THE MARTIN DENNIS COMPANY

Newark, N. J.

DIAMOND ALKALI CHEMICALS

Division of
Diamond Alkali
Company

RESEARCH PAYS DIVIDENDS

when Properly Applied.

RESEARCH LABORATORY
THE TANNER'S COUNCIL
Universtty of Cincinnati

THE TANNERS' COUNCIL RESEARCH LABORATORY
University of Cincinnati

We serve the Tanning and Leather Industry through a broad program of Research.

THAT WILL IMPROVE SPEED OF TANNING—GRAIN TEXTURE—STRENGTH—COLOR PLUMPNESS YIELD?

If so, use the knowledge of an expert in the application of Calgon* to give these improvements in the process of manufacturing and in the quality of your vegetable tanned leathers.

*T.M. Reg. U. S. Pat. Off.

HAGAN · HALL · BUROMIN · CALGON

calgon, inc.

A SUBSIDIARY OF HAGAN CORPORATION

HAGAN BUILDING

INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY VII
AMERICAN DYEWOOD CO. X
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXIV
ARKANSAS COMPANY, INC. VI
ARMOUR LEATHER CO. XXII
ARTHUR C. TRASK CO. XXIX
ARTHUR THOMAS CO. XX
ATLAS REFINERY XVI
BARKEY IMPORTING CO., INC. XXXV
BARIUM REDUCTION CORPORATION XXXIV
BONA ALLEN, INC. XXIV
BUCKMAN LABORATORIES, INC. VIII
BUFFALO EXTRACT & SUPPLY CO. XXXI
CALCO CHEMICAL DIV. XXXII
CALGON, INC. XXXVIII
CLINTON FOODS INC. XXIX
CORN PRODUCTS SALES CO. XXXVI
EISENDRATH TANNING CO. XXV
GENERAL DYESTUFF CORPORATION IX
HADLEY BROS.-UHL COMPANY XXXIII
HOOKER ELECTROCHEMICAL CO. XVII
HOWES LEATHER CO., INC. XXIV
INTERNATIONAL PRODUCTS CORP. XII
KEPEC CHEMICAL CORPORATION XXIX
KEYSTONE TANNING & GLUE CO. XXIX
LEATHER AND SHOES XXX
L. H. LINCOLN & SON, INC. V
MARDEN WILD CORPORATION XIX
MARTIN DENNIS CO., THE XXXVII
MEAD CORPORATION, THE XIII
MUTUAL CHEMICAL CO. OF AMERICA XXII
NEWARK LEATHER FINISH CO. XXXI
NOPCO CHEMICAL CO. XXI
OHIO LEATHER CO., THE XXV
PACIFIC COAST BORAX CO. XXVII
REILLY-WHITEMAN-WALTON CO. XXVII
RIVER PLATE IMPORT AND EXPORT CORPORATION, THE XVIII
ROBESON PROCESS CO. II
ROHM & HAAS XV
SALEM OIL & GREASE CO. XXVIII
SAXE CUTCH CORPORATION XIX
SHOE & LEATHER REPORTER XXVIII
SOCONY-VACUUM OIL CO. I
SOLVAY SALES DIVISION, ALLIED CHEMICAL & DYE CORP. XI
SUN OIL COMPANY XIX
TANEXCO, INC. ..... XL—Inside Back Cover
TANIMEX CORPORATION XXVI
TANNERS' COUNCIL RESEARCH LABORATORY XXXVII
TEAS EXTRACT CO. III
THE LEATHER MANUFACTURER XXIII
THE OLSON SALES AGENCY ..... Inside Front Cover
UNION STARCH & REFINING CO. XXIII
WALLERSTEIN COMPANY, INC. IV
WARNER CO. XXV
WHITTEMORE-WRIGHT CO. XXXI
WOLF, JACQUES & CO. XIV

CHESTNUT

ITALIAN EXTRACT

highest quality — made under
the supervision of the world's
leading extract chemists

CIPEC BRAND

TYPICAL A.L.C.A. ANALYSIS

	Solid	Powder
TANNIN	61.72	66.7
NON-TANNIN	21.65	21.2
INSOLUBLES	.65	.6
WATER	15.98	11.5
ASH	.67	.82

Clean Light Color — Smooth Silky Grain

For further information address:

TANEXCO, INC.

549 W. Washington Blvd. **Chicago 6, Illinois**

SOLE AGENTS
U. S. A.

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

TANNIN	61.55
NON-TANNIN	16.03
INSOLUBLES	1.70
WATER	20.72

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

For further information address:

TANEXCO, INC.

549 WEST WASHINGTON BLVD., CHICAGO 6, ILLINOIS

SOLE AGENTS
U. S. A.

DERMABATE
COMPOUNDS
LIQUID EXTRACTS

HEMLOCK
OAK
MANGROVE
WATTLE
STAINLESS SUMAC
ORDINARY SUMAC
QUEBRACHO
SPECIAL DIPPING EXTRACTS
RAPID TAN "G"

★

AMERICAN EXTRACT CO.

Manufacturers of the Largest
Variety of Vegetable Tanning Extracts
Established 1887
PORT ALLEGANY, PA.

CANADIAN REPRESENTATIVES:
McArthur Chemical Co., Ltd., 20 St. Paul St., West, Montreal: 73 King St., West Toronto

ENGLISH REPRESENTATIVES:
Bay Wilson, Dickson, Ltd., 7-8 Railway Approach, London, S. E. 1